VOL. XLIII. MARCH, 1910. NO. 3.

AMERICAN CHEMICAL JOURNAL

THE CONDUCTIVITIES, DISSOCIATIONS, AND TEMPERATURE COEFFICIENTS OF CONDUCTIVITY BETWEEN 35° AND 80° OF SOLUTIONS OF A NUMBER OF SALTS AND ORGANIC ACIDS.

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[This investigation was carried out with the aid of a grant from the Bache fund, generously awarded to Dr. Jones.]

A large amount of work has been done on the conductivity of solutions of electrolytes at different temperatures. If, however, we consult any compilation of data on this subject, or all of the compilations together, we shall be impressed by the fact that the work in this field has not been systematic, and that the very facts that we most desire are often not available. Again, the range over which conductivity measurements have, for the most part, been made is from 0° to 25°, and frequently the conductivities of a substance have been measured only at one temperature. This often applies to very important compounds.

We measure dissociation usually by the conductivity method, and since chemical activity is so directly connected with dissociation, it is obviously very important that we should know the dissociation of any electrolyte at the temperature

at which it is entering into a chemical reaction. For small ranges in temperature, the dissociation of an electrolyte does not change very greatly, but for even small changes in temperature, the velocity of the ions undergoes very marked change, and the more rapidly the ions move, other things being equal, the greater their chemical activity.

It was with the object of supplying the very important data relative to conductivity at different temperatures, that work was undertaken on this problem in this laboratory nine years ago. Jones and Douglas[1] in 1901 published their paper on "The Association of Certain Acids, Bases and Salts at Different Temperatures." In this work the conductivities of hydrochloric acid, nitric acid, sulphuric acid, potassium hydroxide, sodium hydroxide, potassium chloride, potassium bromide, potassium iodide, potassium nitrate, sodium nitrate, ammonium nitrate, potassium sulphate, and potassium permanganate, at dilutions ranging from normal to several thousandths normal, were measured, and from these results the dissociations at the various temperatures calculated. The conductivities were measured at 0° as the lowest temperature, and 35° as the highest, also at 25° and at the temperature of hydrant water, which was usually around 10° to 15°. From this earlier work the conclusion was drawn that the temperature coefficient of conductivity increases with the dilution of the solution. For salts, the temperature coefficient increases with rise in temperature, but for acids and bases there is very little change in the coefficient with temperature.

It was shown in this earlier work that for the range of temperature studied, the dissociation did not change to any great extent. It was pointed out that this is in accord with the approximate agreement between the dissociation as measured by the freezing point method by Jones[2] and the dissociation as determined by the Kohlrausch conductivity method. The former results were obtained at temperatures slightly below 0°, while the latter were obtained at 18°.

[1] This Journal, **26**, 428 (1901).
[2] Z. physik. Chem., **11**, 110, 529; **12**, 623 (1893).

The method of making the conductivity measurements was greatly improved after this earlier work was done. A large number of details were worked out, and some sources of error in the earlier work eliminated or reduced to a minimum. The next work on this problem was undertaken in 1904 and published in 1905[1] by Jones and West. This investigation extended over the same range of temperature as that of Jones and Douglas, *viz.*, from 0° to 35°. They worked with solutions of ammonium chloride, ammonium bromide, sodium bromide, sodium iodide, sodium carbonate, sodium acetate, potassium chloride, potassium bromide, potassium iodide, potassium nitrate, potassium sulphate, potassium bisulphate, potassium carbonate, potassium ferrocyanide, calcium chloride, calcium bromide, strontium bromide, barium chloride, magnesium chloride, zinc sulphate, manganese chloride, manganese nitrate, cobalt chloride, cobalt nitrate, nickel chloride, nickel nitrate, copper chloride, copper nitrate, hydrochloric acid, nitric acid, sulphuric acid, and oxalic acid. The concentrations used ranged from a volume of two to that of over eight thousand. The temperatures were 0°, that of the hydrant water, 25° and 35°. A number of improvements in the method as earlier used were made and the results obtained are more accurate than those in the earlier work. It was found that over the range in temperature between 0° and 35° the dissociation decreased with rise in temperature. This is in accord with the investigations of Noyes[2] and coworkers at higher temperatures. It was also shown that the percentage temperature coefficients of conductivity decrease with rise in temperature from 0° to 35°.

It was pointed out that these facts are of interest in connection with certain theories that have been proposed, connecting the dissociating power and certain other physical properties of solvents. Thus, Dutoit and Aston[3] showed that the more associated a solvent the greater its dissociating power, and while this relation is not quantitative, there is undoubtedly a large element of truth in it. With rise in tem-

[1] This Journal, **34**, 357 (1905).
[2] Monograph No. 63, Carnegie Institution of Washington.
[3] Compt. Rend., **125**, 540 (1897).

perature the association of liquids becomes less and less and their dissociating power becomes smaller.

The results obtained are also in accord with the Thomson[1]–Nernst[2] hypothesis, connecting the dielectric constants of solvents with their dissociating power. The dielectric constants of solvents decrease with rise in temperature, and the dissociating power of solvents decreases with rise in temperature. Theory and fact are thus in perfect accord.

The next investigation was on the conductivity and ionization of electrolytes in aqueous solutions as conditioned by temperature, dilution and hydrolysis, by Jones and Jacobson.[3] The methods earlier used were still further improved, and the following compounds studied: Lithium chloride, lithium bromide, lithium nitrate, lithium sulphate, sodium nitrate, disodium phosphate, potassium sulphocyanate, potassium chromate, potassium dichromate, calcium nitrate, strontium chloride, strontium nitrate, strontium formate, barium bromide, barium nitrate, barium formate, barium acetate, magnesium sulphate, cupric bromide, chromium chloride, chromium nitrate, ferric chloride, ferric nitrate, nickel sulphate, nickel acetate, cobalt sulphate, cobalt acetate, lead nitrate, trichloracetic acid, racemic acid, picric acid, propionic acid, *o*-nitrobenzoic acid, and *m*-nitrobenzoic acid.

The range of dilution was usually from volume 2 to volume 2048. Occasionally higher dilutions were employed. The range of temperature was from 0° to 35°, the conductivities being measured also at 25°, and at a temperature that was not far from 10°. Results of the same general character were obtained as in the earlier investigations. It was shown that conductivity is not a linear function of the temperature at any dilution worked with, the increase in conductivity with rise in temperature being greater the higher the temperature. The conductivities are parabolic functions of the temperature. The importance of hydrolysis as affecting conductivity is also pointed out. The temperature coefficients of conductivity of a number of organic acids have been

[1] Phil. Mag., **36**, 320 (1894).
[2] Z. physik. Chem., **13**, 531 (1894).
[3] This Journal, **40**, 355 (1908).

measured in this laboratory by Mr. G. F. White, and some of the results have been published in THIS JOURNAL.[1]

A number of relations between the temperature coefficients of conductivity and the present hydrate theory were pointed out by Jones.[2] Since most of the ions are hydrated and since the complexity of the hydrate decreases with rise in temperature, the mass of the ion would decrease with rise in temperature. Therefore, if everything else remained unchanged the conductivity would increase from this cause alone. We should, then, expect to find that *those ions which have the largest hydrating power would have the largest temperature coefficients of conductivity.* That such is the case has already been shown to be the fact.[3]

Since the complexity of the hydrate is greater the higher the dilution, we should expect a greater change in the complexity of the hydrate with change in temperature at higher than at lower dilutions. In a word, *the temperature coefficient of conductivity for any given substance is greater at a high than at a low dilution.* This conclusion is also established by the facts.[4]

The large change in conductivity with rise in temperature is due, then, in part to *the decreasing complexity of the hydrates formed around the ions.* If other things remained equal, this would cause the ions to move faster through the solvent.

It is, of course, at the same time true that, with rise in temperature, the solvent is becoming less viscous, and this also would increase the velocity of the ions.

The object of the present investigation is to extend the earlier work from 35° to as high temperature as can be employed with solutions in ground-glass stoppered vessels. We find that we can work very satisfactorily up to 65° when we take sufficient precautions. The more concentrated solutions can be studied even up to 80°.

It seems to us to be a matter of very considerable importance for chemistry to know the conductivity of solutions over the

[1] **42,** 520 (1909).
[2] THIS JOURNAL, **34,** 357 (1905).
[3] *Ibid.*, **35,** 448 (1906); **40,** 404 (1908).
[4] *Ibid.*, **35,** 449 (1906).

range in temperature indicated above, since so many chemical reactions take place and so much chemical work is done within these temperature limits. Further, when we examine the literature we find that comparatively few reliable conductivity measurements have been made over this temperature range, and where such measurements have been made the temperatures chosen have been so far apart that we cannot calculate the temperature coefficients for any narrow range in temperature with any high degree of accuracy.

It is with the idea of supplying these data that the present work was done, and we intend to include within its scope practically all of the more important inorganic and organic compounds.

EXPERIMENTAL PART.

Apparatus.

The cells used were of the same general type as those employed in previous investigations on a similar problem in this laboratory and described by Jones and Lindsay[1] and Jones and West[2]. The ground-glass stoppers of the cells were hollow, the upper and lower surfaces being about 3 cm. apart. The hollow glass tubes carrying the electrodes were sealed directly into the stoppers, since the use of sealing wax, which had been previously employed for holding the electrode tubes in place, was inadmissible at the temperatures to which the cells were subjected in this work. The electrodes were coated with platinum black and then heated in the blast lamp. Seven or eight cells were used, each cell being employed regularly for a certain strength of solution. The distance separating the electrodes varied from about 4.5 cm. in the case of the cell used in measuring the most concentrated solutions to about 3.5 mm. in the case of the cell used for the most dilute solutions.

The Kohlrausch method involving the use of an ordinary Wheatstone bridge was employed. The bridge wire, resistance box and the thermometers used in regulating the temperatures of the baths were all calibrated in the same way

[1] THIS JOURNAL, **28**, 329 (1902).
[2] *Ibid.*, **34**, 336 (1905).

as that described by previous workers in this laboratory.

Measurements were made at four different temperatures, namely, 35°, 50°, 65° and 80°. For thermostats, two galvanized tubs were used, each having a capacity of 25 or 30 liters. These were heated with a gas flame regulated by hand and the water was stirred by means of a motor. The bath used for measurements at 35° and 50° was protected on the sides by a sheet of thick asbestos. The other bath, which was used in working at 65° and 80°, was in addition protected on the bottom by a sheet of thick asbestos, in which a small hole was made for heating. The sides of this vessel were double walled, the intermediate space being packed with finely divided asbestos and magnesia. It was an easy matter to maintain a constant temperature in these baths to within 0°.05 during the time required to bring the cell contents to temperature equilibrium and make the necessary readings.

It was possible to immerse the cells in the bath almost completely, but as the cells were nearly filled with the solution, it was desirable to maintain the air above the water of the bath at a temperature as near that of the bath as practicable. With the bath at 35° this difference in temperature is inconsiderable, but for higher temperatures, two rectangular pieces of glass were used for a covering, each being placed over one-half of the bath. The stirrer and the thermometer passed between these two plates. A number of circular holes were cut in the glass plates at the proper places so that the copper wires used in making connection with the cells could be introduced from the outside without any trouble. The mercury cups used in connecting these wires were movable and were placed on top of the glass cover. The plates were elevated slightly at the edges of the bath so that the water which condensed upon the plates ran toward the middle and dropped back into the bath. This arrangement was found to be very convenient and entirely satisfactory. At 80° the temperature of the air space above the water was only about 15° lower than that of the bath and at the other temperatures the difference was considerably less.

Preparation of Solutions.

The chemicals used were all obtained from the firm of C. A. F. Kahlbaum. In every case the purest obtainable substance was used and this was further purified by several recrystallizations. Where other methods of purification or preparation were employed they will be described in detail under the heading of the given substance. Unless otherwise specified the salts used were first dried in a desiccator after recrystallization, then pulverized and dried to constant weight in an air bath at 170°. The ammonium salts were treated in the same manner, but were dried at 100°. All purified substances were preserved until used in glass-stoppered bottles placed in a desiccator. Wherever possible the 0.5 gram-molecular solution, which was the highest concentration used, was made by directly weighing the substance. Where this was not possible the substance was dissolved in water and its concentration determined by analysis; from this stock solution the required amount (from 75 cc. to 100 cc.) was measured by means of a calibrated 100 cc. burette.

Since the coefficient of expansion of water increases greatly with the temperature, it was necessary to take care in regard to having the solutions made at the *exact temperature* at which they were to be measured or to applying the proper correction. The solutions measured at 50°, 65° and 80° were prepared at these temperatures, respectively. The solutions prepared at 50° were also used for the measurements at 35°, and the correction factor 0.994 was then applied to all dilutions except the 0.5 gram-molecular solutions, for which the factor 0.993 was used.[1]

From the solution of greatest concentration all the others were prepared by dilution, by means of pipettes and measuring flasks. All of the measuring vessels employed were carefully calibrated by means of pure water, and the weights reduced to a vacuum. The water used for the solutions was prepared in the manner described by previous workers in this laboratory, and it had a conductivity varying from 1.5

[1] Landolt–Börnstein: Physikalisch-chemische Tabellen, Berlin, 1905.

to 2.0×10^{-6}. The correction which must be applied for the conductivity of the water is of course much larger at higher temperatures, and was carefully determined in duplicate, in two cells, just before the measurement of the solutions.

Cell Constants.

The greatest obstacle which has been encountered in this work relates to the constants of the cells.

It has developed that a strain is brought about by the high temperatures which may result in a change either in the distance of the electrode plates from each other or in the surface of the plates. Naturally, these changes are manifested chiefly in those cells in which the electrodes are relatively close together. The electrodes have been removed and again sealed into the glass, and have also been again ignited in the blast lamp, but the same behavior has persisted.

Since such a variation had not previously been observed in work covering a range from 0° to 35°, it was thought that the changes might be reduced by maintaining the cells at a temperature which was about a mean of those employed in the experimental work. Accordingly, when not in use, the cells were filled with pure water and placed in a bath which was maintained continuously at a temperature of 45° to 50°. Although this procedure was continued for several months, it was found that the changes were not entirely prevented, although they were not as frequent as they had previously been. It was due largely to this cause that no measurements of the more dilute solutions at 80° were attempted in these cells.

The changes in the value of the cell constant just considered sometimes amounted to one per cent. The constants were measured at least once a week throughout the course of this work, and it is by this means that it has been possible to secure fairly accurate results in the case of the dilute solutions, since all variations have been quickly noted and by taking a mean of the two values the error has been reduced to a minimum.

Some other interesting results have been obtained which

bear upon the strict reliability of the cell constants when used at elevated temperatures with dilute solutions. A series of measurements was arranged which should serve as a check upon the accuracy of the entire procedure followed regularly in obtaining the results described and recorded in this paper. There are several possible sources of error, such as the solubility of the glass and the effect of the solute upon the glass, the evaporation of the solvent, the presence of air bubbles, and other errors due to difficulties in manipulation at an elevated temperature. Most of the possible sources of error concern only the dilute solutions. Accordingly several different substances were measured at 3 dilutions (5, 1024 and 2048) in the cells ordinarily used for solutions of this strength. The measurements were first carefully made at 35° and duplicated, then the regular systematic procedure was gone through at 65°, and after this readings at 35° were again made. If the results obtained the second time should agree with those first obtained at 35°, this would be strong evidence that the method was reliable. It was found that in over one-half the cases at 80° the second reading differed slightly from the first. In other cases there was no difference, and the change appeared to be independent of the cell used, or the concentration of the solution. It was found, further, that on standing for a considerable length of time at 35° (2 or 3 hours) *the reading slowly changed back in all cases to the original value.* Although these changes amount to less than 3 mm. on the bridge this was sufficient to cause the difference referred to, and is greater than any possible error in the reading. It is difficult to see what other cause can be assigned to these results than a temporary change in the cell constant during the heating at 65°.

In determining the cell constants, a 0.02 N solution of potassium chloride was employed for those cells used in measuring the stronger solutions and a 0.002 N normal solution of the same substance for the remaining cells. The value 129.7 for μ_v 25° for the 0.02 N potassium chloride solution was used, and from this the mean value 137.5 was found, as the result of several experiments, for μ_v 25° for the 0.002 N solu-

tion. This is in good agreement with 137.7, the value obtained by Jacobson.[1]

Solubility of Glass.

In conductivity work at ordinary temperatures this factor has always been neglected, and probably is not sufficiently large to influence the results even with very dilute solutions. However, at 50° the error introduced by this factor at a dilution of 1000 is greater than any of the other ordinary experimental errors. At 65° the solubility of the glass is still greater, and at 80° the conductivity of pure water is increased tenfold on remaining in the cell for a couple of hours. In this connection it may be stated that the cells employed were made of hard glass. Of course, the amount of glass dissolved depends upon the exact nature of the latter and was found to vary considerably with the different cells used, and at different intervals in the case of any one cell. The idea of introducing a correction for the solubility of the glass was abandoned but the difficulty was overcome in another way. It was found that after the cells had been heated with water for several days the amount of glass dissolved gradually decreased and finally amounted to practically nothing. After this treatment, as the cells were kept in a bath at 45° to 50° and the water in them changed once a day, the solubility of the glass at 65° was always practically nothing, or entirely negligible. If a cell were removed from the bath and allowed to stand filled with water at the room temperature for any length of time, it was found that glass was again dissolved on heating, It is quite certain that this factor does not stand in the way of very accurate work at 65°, but at 80° the question was not studied on account of the changes in the cell constants, which has already been discussed.

Procedure.

A number of difficulties in manipulation were encountered at the beginning, and it was only after some experience and practice that it was possible to do careful work with the desirable rapidity.

[1] THIS JOURNAL, **40**, 364 (1908).

At a temperature of 25° or lower the formation of air bubbles upon the plates is so slight that they may be entirely neglected. At 35° there is a noticeable formation of bubbles during the 20 or 30 minutes required for complete temperature equilibrium. At 50° and 65° the bubbles are much more abundant. If, however, at these latter temperatures, the cells are allowed to remain in the bath for nearly an hour, the formation of bubbles ceases, and if the bubbles are removed by taking out the cell and agitating the solution, no more appear. For this reason, it was necessary in working at 50° and 65° to allow all solutions to remain in the bath for an hour before proceeding farther. At 80° the formation of bubbles ceases in much less time.

For several reasons the cells were nearly filled with the solution: First, to minimize any slight change in concentration brought about by condensation or escape of the solvent, or from any other cause. Second, to exclude the air with its accompanying carbon dioxide from the cell, as the dioxide would be dissolved during the manipulation and would influence the results with dilute solutions. Third, to prevent difficulty in opening the cells. With a large air space diminished pressure is quickly produced on removal from the bath, and if the cells can be opened at all it can be done only at the risk of distorting the electrodes.

After the formation of bubbles had ceased and the solutions had been gently agitated to clear the plates, the cells were replaced in the bath and readings made as soon as temperature equilibrium had been reached. The entire procedure, including the removal of the cell and agitation of the solution, was then repeated as a check upon the first.

After the measurements at 50° had been completed the bath was cooled to 35°, and without changing the solution measurements were made and duplicated at the latter temperature. In this way it was possible to use one set of solutions for both temperatures, and the difficulty with air bubbles encountered on measuring directly at 35° was entirely avoided. It was necessary to heat the cells again to 50° or above in order to open them. When not in use the cells

which were not kept in the bath at 45° to 50° were filled with pure water.

Units.

In conformity with previous work of this nature published from this laboratory the conductivity values are expressed in Siemens units, and the molecular conductivities in all cases refer to gram molecules of the substances.

Lithium Chloride.

The salt was recrystallized once and was then dissolved in water. The lithium in this solution was determined as the sulphate and the 0.5 gram-molecular solution was prepared from it by volume.

Table I.—Molecular Conductivity and Percentage Dissociation.

	35°.		50°.		65°.	
V.	μ_v.	α.	μ_v.	α.	μ_v.	α.
2	92.34	69.9	117.7	69.4	144.1	68.4
8	107.2	81.1	136.7	80.6	167.7	79.6
32	116.7	88.3	149.8	88.4	185.6	88.1
128	124.1	93.9	159.3	94.0	199.0	94.5
512	128.6	97.3	165.2	97.5	205.3	97.5
1024	130.2	98.6	167.5	98.8	208.3	98.9
2048	132.1	100.0	169.5	100.0	210.6	100.0

Table II.—Temperature Coefficients.

	35° to 50°.		50° to 65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	1.69	1.83	1.76	1.50
8	1.97	1.84	2.07	1.51
32	2.21	1.89	2.39	1.60
128	2.35	1.89	2.65	1.66
512	2.44	1.90	2.67	1.62
1024	2.49	1.91	2.72	1.62
2048	2.49	1.88	2.74	1.62

Sodium Chloride.

The salt was purified by precipitation from solution with hydrochloric acid gas, recrystallization from dilute hydrochloric acid, and a final recrystallization from pure water.

Table III.—Molecular Conductivity and Percentage Dissociation.

	35°.		50°.		65°.		
V.	μ_v.	α.	μ_v.	α.	μ_v.	α.	$\mu_v 80°$.
2	104.6	72.4	132.6	71.8	161.8	70.8	191.8
8	118.3	81.9	150.5	81.5	184.5	80.7	220.1
32	129.0	89.3	164.3	89.0	201.0	88.0	242.0
128	137.2	95.0	175.4	95.0	214.7	94.0	256.2
512	141.6	98.1	181.1	98.0	222.9	97.5	...
1024	143.4	99.3	183.2	99.2	225.5	98.7	...
2048	144.4	100.0	184.7	100.0	228.5	100.0	...

Table IV.—Temperature Coefficients.

	35° to 50°.		50° to 65°.		65° to 80°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	1.87	1.79	1.95	1.47	2.00	1.24
8	2.15	1.82	2.27	1.51	2.37	1.28
32	2.35	1.82	2.45	1.49	2.73	1.36
128	2.55	1.86	2.62	1.49	2.77	1.29
512	2.63	1.86	2.79	1.54	..	..
1024	2.65	1.85	2.82	1.54	..	..
2048	2.69	1.86	2.92	1.58	..	..

Sodium Bromide.

Table V.—Molecular Conductivity and Percentage Dissociation.

	35°.		50°.		65°.		
V.	μ_v.	α.	μ_v.	α.	μ_v.	α.	$\mu_v 80°$.
2	106.25	74.7	131.1	72.0	162.6	71.6	196.2
8	119.2	83.8	151.4	83.2	184.1	81.1	222.6
32	129.1	90.7	164.5	90.4	201.0	88.5	243.7
128	136.7	96.1	174.6	95.9	212.6	93.7	259.6
512	140.5	98.7	180.1	98.9	219.5	96.7	...
1024	141.4	99.4	180.9	99.4	222.8	98.2	...
2048	142.3	100.0	182.0	100.0	227.0	100.0	...

Table VI.—Temperature Coefficients.

	35° to 50°.		50° to 65°.		65° to 80°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	1.66	1.56	2.10	1.60	2.24	1.38
8	2.15	1.80	2.18	1.44	2.57	1.40
32	2.36	1.83	2.43	1.48	2.85	1.42
128	2.53	1.85	2.53	1.45	3.13	1.47
512	2.64	1.88	2.63	1.46	..	..
1024	2.63	1.86	2.79	1.54	..	..
2048	2.65	1.86	3.00	1.65	..	..

Sodium Nitrate.

Table VII.—Molecular Conductivity and Percentage Dissociation.

	35°.		50°.		65°.		
V.	μ_v.	α.	μ_v.	α.	μ_v.	α.	μ_v80°.
2	95.05	69.2	120.1	68.5	146.0	68.5	173.5
8	111.3	81.1	141.1	80.5	171.4	80.4	203.6
32	122.8	89.4	155.7	88.9	189.0	88.6	225.4
128	129.6	94.4	164.8	94.1	201.3	94.4	241.8
512	134.4	97.9	171.0	97.6	209.6	98.3	...
1024	135.8	98.9	173.1	98.8	213.2	100.0	...
2048	137.3	100.0	175.2	100.0	213.2	100.0	...

Table VIII.—Temperature Coefficients.

	35° to 50°.		50° to 65°.		65° to 80°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	1.67	1.76	1.73	1.44	1.83	1.25
8	1.99	1.79	2.02	1.43	2.15	1.25
32	2.19	1.78	2.22	1.43	2.43	1.29
128	2.35	1.81	2.43	1.47	2.70	1.34
512	2.44	1.82	2.57	1.50	..	..
1024	2.49	1.83	2.67	1.54	..	..
2048	2.53	1.84	2.53	1.44	..	..

Sodium Sulphate.

The purified salt was pulverized and dried to constant weight at 150°.

Table IX.—Molecular Conductivity and Percentage Dissociation.

	35°.		50°.		65°.		
V.	μ_v.	α.	μ_v.	α.	μ_v.	α.	μ_v80°.
2	134.5	46.1	172.5	45.9	205.4	43.8	248.1
8	173.7	59.5	221.8	59.0	274.3	58.5	331.9
32	204.6	70.1	262.2	69.7	337.2	71.9	410.7
128	233.1	79.9	320.4	85.2	399.0	85.1	474.3
512	273.6	93.8	353.2	93.9	437.9	93.4	...
2048	288.0	98.7	372.6	99.1	462.5	98.7	...
4096	291.8	100.0	376.0	100.0	468.7	100.0	...

Table X.—Temperature Coefficients.

	35° to 50°.		50° to 65°.		65° to 80°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	2.53	1.88	2.19	1.27	2.85	1.39
8	3.21	1.85	3.50	1.58	3.84	1.40
32	3.84	1.88	5.00	1.91	4.90	1.45
128	5.82	2.50	5.24	1.64	5.02	1.26
512	5.31	1.94	5.65	1.60	..	..
2048	5.64	1.96	5.99	1.61	..	..
4096	5.61	1.92	6.18	1.64	..	..

Potassium Chloride.

Table XI.—Molecular Conductivity and Percentage Dissociation.

	35°.		50°.		65°.		
V.	μ_v.	α.	μ_v.	α.	μ_v.	α.	$\mu_v 80°$.
2	129.6	77.4	161.9	76.3	193.7	76.4	226.5
8	142.5	85.1	179.1	84.4	215.9	83.3	254.4
32	152.8	91.2	192.8	90.9	234.1	90.3	277.4
128	161.9	96.7	204.3	96.3	247.1	95.3	292.8
512	165.6	98.9	209.1	98.6	255.8	98.6	...
1024	167.7	100.1	211.6	99.8	258.3	99.6	...
2048	167.5	100.0	212.1	100.0	259.3	100.0	...

Table XII.—Temperature Coefficients.

	35° to 50°.		50° to 65°.		65° to 80°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	2.15	1.66	2.12	1.31	2.19	1.13
8	2.44	1.71	2.45	1.37	2.57	1.19
32	2.67	1.75	2.75	1.43	2.89	1.23
128	2.83	1.75	2.85	1.40	3.05	1.23
512	2.90	1.75	3.11	1.49	..	..
1024	2.93	1.75	3.11	1.47	..	..
2048	2.97	1.77	3.15	1.49	..	..

Potassium Bromide.

Table XIII.—Molecular Conductivity and Percentage Dissociation.

	35°.		50°.		65°.		
V.	μ_v.	α.	μ_v.	α.	μ_v.	α.	$\mu_v 80°$.
2	133.2	77.7	165.1	76.2	196.7	74.6	231.6
8	145.4	84.8	181.4	83.7	218.1	82.7	257.8
32	155.6	90.8	195.3	90.1	236.5	89.7	280.9
128	164.2	95.8	206.0	95.1	250.0	94.8	300.0
512	167.7	97.8	211.6	97.6	256.6	97.3	...
1024	169.0	98.6	213.6	98.6	260.3	98.7	...
2048	171.4	100.0	216.7	100.0	263.7	100.0	...

Table XIV.—Temperature Coefficients.

	35° to 50°.		50° to 65°.		65° to 80°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	2.13	1.60	2.11	1.28	2.33	1.18
8	2.40	1.65	2.45	1.35	2.65	1.22
32	2.65	1.70	2.75	1.41	2.96	1.25
128	2.79	1.70	2.93	1.42	3.33	1.33
512	2.93	1.75	3.00	1.42	..	..
1024	2.97	1.76	3.11	1.46	..	..
2048	3.02	1.76	3.13	1.45	..	..

Potassium Nitrate.

Table XV.—Molecular Conductivity and Percentage Dissociation.

	35°.		50°.		65°.		
V.	μ_v.	α.	μ_v.	α.	μ_v.	α.	μ_v80°.
2	113.2	70.4	141.3	69.8	170.0	69.0	205.1
8	131.8	81.9	165.0	81.5	199.6	81.0	236.9
32	145.3	90.3	182.0	89.9	220.4	89.4	260.2
128	154.7	96.1	194.1	95.9	235.4	95.5	278.6
512	159.1	98.9	199.8	98.7	242.1	98.3	...
1024	161.2	100.2	202.7	100.1	245.2	99.5	...
2048	160.9	100.0	202.5	100.0	246.1	100.0	...

Table XVI.—Temperature Coefficients.

	35° to 50°.		50° to 65°.		65° to 80°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	1.87	1.65	1.91	1.35	2.34	1.38
8	2.21	1.68	2.31	1.40	2.49	1.25
32	2.45	1.69	2.56	1.41	2.65	1.20
128	2.63	1.70	2.75	1.42	2.88	1.22
512	2.71	1.70	2.82	1.41	..	..
1024	2.77	1.72	2.83	1.40	..	..
2048	2.77	1.72	2.91	1.44	..	..

Potassium Sulphate.

Table XVII.—Molecular Conductivity.

V.	μ_v 35°.	μ_v 50°.	μ_v 65°.	μ_v 80°.
2	181.1	224.8	267.2	307.7
8	220.3	276.7	332.8	390.8
32	259.7	329.2	400.0	473.1
128	296.9	376.0	456.2	547.7
512	319.6	406.7	500.7	...
1024	328.2	419.6	513.1	...

Table XVIII.—Temperature Coefficients.

	35° to 50°.		50° to 65°.		65° to 80°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	2.91	1.61	2.83	1.26	2.70	1.01
8	3.76	1.71	3.74	1.35	3.87	1.16
32	4.63	1.78	4.72	1.43	4.87	1.22
128	5.27	1.77	5.35	1.42	6.10	1.34
512	5.81	1.82	6.27	1.54	..	..
1024	6.09	1.86	6.23	1.48	..	..

Potassium Chromate.

Table XIX.—Molecular Conductivity.

V.	μ_v 35°.	μ_v 50°.	μ_v 65°.
2	200.5	249.1	295.9
8	237.3	297.5	357.7
32	272.7	343.8	417.4
128	307.9	389.4	468.5
512	326.7	415.0	513.6

Table XX.—Temperature Coefficients.

	35° to 50°.		50° to 65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	3.24	1.62	3.12	1.25
8	4.01	1.69	4.01	1.35
32	4.74	1.74	4.91	1.43
128	5.43	1.76	5.27	1.35
512	5.89	1.80	6.57	1.58

Potassium Acetate.

The salt was prepared by neutralizing a quantity of acetic acid with the best quality of potassium hydroxide from alcohol, evaporating to dryness and then dissolving the product in water and neutralizing with a small additional amount of acetic acid. The acetic acid used was recrystallized twice by cooling, and was then dissolved in water and the strength of the solution determined as in the case of oxalic acid (see p. 210). The exact amount of acetic acid used in preparing the salt was accordingly known and the solution of the salt was brought to a definite volume and used in preparing the solution for measurement.

Table XXI—Molecular Conductivity and Percentage Dissociation.

	35°.		50°.		65°.	
V.	μ_v.	α.	μ_v.	α.	μ_v.	α.
4	101.7	77.9	129.2	77.5	157.4	74.7
16	113.7	87.1	144.6	86.7	177.1	84.0
64	121.7	93.3	155.0	93.0	190.4	90.3
256	127.0	97.3	162.3	97.4	199.7	94.7
1024	129.4	99.2	165.1	99.0	203.7	96.6
2048	130.5	100.0	166.7	100.0	210.8	100.0

Table XXII.—Temperature Coefficients.

	35° to 50°.		50° to 65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
4	1.83	1.80	1.88	1.46
16	2.06	1.81	2.17	1.50
64	2.22	1.82	2.36	1.52
256	2.35	1.85	2.49	1.53
1024	2.38	1.84	2.57	1.56
2048	2.41	1.85	2.94	1.76

Potassium Benzoate.

The salt was prepared from a weighed quantity of pure benzoic acid in exactly the same way as potassium acetate. The benzoic acid was purified by recrystallizing several times from water, pulverizing and drying *in vacuo*.

Table XXIII.—Molecular Conductivity and Percentage Dissociation.

	35°.		50°.		
V.	μ_v.	α.	μ_v.	α.	$\mu_v 65°$.
16	102.5	85.9	131.1	86.1	160.4
32	107.5	90.1	137.0	90.0	167.3
64	110.9	93.0	141.6	93.0	173.2
128	114.7	96.1	146.7	96.3	...
512	118.6	99.4	151.1	99.2	...
1024	119.3	100.0	152.3	100.0	...

Table XXIV.—Temperature Coefficients.

	35° to 50°.		50° to 65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
16	1.91	1.86	1.95	1.49
32	1.97	1.83	2.02	1.47
64	2.05	1.85	2.11	1.49
128	2.13	1.86	..	...
512	2.17	1.83	..	...
1024	2.20	1.84	..	...

Ammonium Chloride.

Table XXV.—Molecular Conductivity and Percentage Dissociation.

	35°.		50°.		65°.		
V.	μ_v.	α.	μ_v.	α.	μ_v.	α.	μ_v 80°.
2	129.2	75.2	161.4	73.9	194.0	73.1	227.7
8	142.3	82.8	179.4	82.2	217.1	81.8	256.5
32	153.2	89.1	194.0	88.9	235.9	88.9	279.3
128	162.8	94.7	206.2	94.4	251.1	94.6	296.4
512	166.8	97.0	211.4	96.8	259.5	97.8	...
1024	169.0	98.3	214.4	98.2	269.7	101.6	...
2048	171.9	100.0	218.3	100.0	265.4	100.0	...

Table XXVI.—Temperature Coefficients.

	35° to 50°.		50° to 65°.		65° to 80°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	2.15	1.66	2.17	1.34	2.25	1.16
8	2.47	1.74	2.51	1.40	2.63	1.21
32	2.72	1.78	2.79	1.44	2.89	1.23
128	2.89	1.78	2.99	1.45	3.02	1.20
512	2.97	1.78	3.21	1.52	..	..
1024	3.03	1.79	3.69	1.72	..	..
2048	3.09	1.80	3.14	1.44	..	..

Ammonium Nitrate.

Table XXVII.—Molecular Conductivity and Percentage Dissociation.

	35°.		50°.		65°.	
V	μ_v.	α.	μ_v.	α.	μ_v.	α.
2	119.5	73.2	148.9	72.5	179.8	71.5
8	135.2	82.8	169.3	82.5	204.3	81.2
32	146.4	89.7	184.2	89.7	223.0	88.6
128	154.9	94.9	195.2	95.1	237.5	94.4
512	158.9	97.4	201.4	98.1	246.3	97.9
1024	160.2	98.2	203.7	99.2	249.3	99.1
2048	163.2	100.0	205.3	100.0	251.6	100.0

Table XXVIII.—Temperature Coefficients.

	35° to 50°.		50° to 65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	1.96	1.64	2.06	1.38
8	2.27	1.68	2.33	1.38
32	2.52	1.72	2.59	1.41
128	2.69	1.74	2.82	1.44
512	2.83	1.78	2.99	1.48
1024	2.90	1.81	3.04	1.49
2048	2.81	1.72	3.09	1.51

Ammonium Sulphate.

Table XXIX.—Molecular Conductivity.

V.	μ_v 35°.	μ_v 50°.	μ_v 65°	μ_v 80°.
2	172.8	215.8	257.6	300.1
8	215.1	270.8	325.2	381.1
32	256.3	324.3	393.3	465.2
128	295.7	375.8	461.7	537.1
512	326.3	417.0	506.5	...
2048	335.0	428.4	528.2	...
4096	344.1	440.0	538.6	...

Table XXX.—Temperature Coefficients.

	35° to 50°.		50° to 65°.		65° to 80°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	2.87	1.66	2.79	1.29	2.83	1.10
8	3.71	1.72	3.63	1.34	3.73	1.15
32	4.53	1.77	4.60	1.42	4.79	1.22
128	5.34	1.81	5.73	1.52	5.03	1.09
512	6.05	1.85	5.97	1.43	..	..
2048	6.23	1.86	6.65	1.55	..	..
4096	6.39	1.86	6.57	1.49	..	..

Barium Chloride.

The recrystallized salt was dried in a desiccator, then pulverized and dried to constant weight in an air bath at 150°.

Table XXXI.—Molecular Conductivity.

V.	μ_v 35°.	μ_v 50°.	μ_v 65°.	μ_v 80°.
2	176.4	220.6	259.8	310.2
8	216.0	272.4	322.3	387.3
32	247.6	313.9	375.3	455.1
128	274.2	348.7	421.5	509.2
512	295.7	378.0	453.8	...
2048	308.4	395.0	478.0	...

Table XXXII.—Temperature Coefficients.

	35° to 50°.		50° to 65°.		65° to 80°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	2.95	1.67	2.61	1.18	3.36	1.29
8	3.76	1.74	3.33	1.22	4.33	1.34
32	4.42	1.79	4.09	1.30	5.32	1.42
128	4.97	1.81	4.85	1.39	5.85	1.39
512	5.49	1.86	5.05	1.34	..	..
2048	5.77	1.87	5.53	1.40	..	..

Barium Nitrate.

The recrystallized substance was dissolved in water and the barium in this solution estimated as the sulphate.

Table XXXIII.—Molecular Conductivity and Percentage Dissociation.

	35°.		50°.		65°.	
V.	μ_v.	α.	μ_v.	α.	μ_v.	α.
8	177.3	58.3	226.1	59.1	276.2	58.1
32	221.6	72.9	282.0	73.8	344.2	72.4
128	256.4	84.4	325.5	85.1	398.3	83.8
512	283.8	93.4	360.7	94.3	440.7	92.7
2048	299.4	98.5	378.4	99.0	467.0	98.2
4096	303.9	100.0	382.3	100.0	475.5	100.0

Table XXXIV.—Temperature Coefficients.

	35° to 50°.		50° to 65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
8	3.25	1.83	3.34	1.48
32	4.03	1.82	4.15	1.47
128	4.61	1.80	4.85	1.49
512	5.13	1.81	5.33	1.48
2048	5.27	1.76	5.91	1.56
4096	5.23	1.72	6.21	1.62

Magnesium Nitrate.

The recrystallized salt was dissolved in water and the magnesium in this solution determined as the sulphate. The 0.5 gram-molecular solution was then prepared by volume.

Table XXXV.—Molecular Conductivity.

V.	μ_v 35°.	μ_v 50°.	μ_v 65°.
2	154.5	193.7	234.8
8	193.6	244.5	298.1
32	223.2	283.5	347.4
128	249.2	316.8	390.8
512	266.9	341.6	421.1
2048	278.5	357.0	443.4

Table XXXVI.—Temperature Coefficients.

	35° to 50°.		50° to 65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	2.61	1.69	2.74	1.41
8	3.39	1.75	3.57	1.46
32	4.02	1.80	4.26	1.50
128	4.51	1.81	4.93	1.56
512	4.98	1.87	5.30	1.55
2048	5.23	1.88	5.76	1.61

Magnesium Sulphate.

The recrystallized salt was dried in a desiccator, then pulverized and the percentage of anhydrous salt in the product determined by ignition.

Table XXXVII.—Molecular Conductivity.

V.	μ_v 35°.	μ_v 50°.	μ_v 65°.
2	74.20	92.61	109.2
8	105.7	131.5	155.0
32	140.6	175.7	208.4
128	185.1	234.0	282.7
512	230.7	295.7	358.9
2048	268.4	347.0	427.2
4096	282.0	365.0	446.3

Table XXXVIII.—Temperature Coefficients.

	35° to 50°.		50° to 65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	1.23	1.66	1.11	1.20
8	1.72	1.63	1.57	1.19
32	2.34	1.66	2.18	1.24
128	3.26	1.76	3.25	1.39
512	4.33	1.88	4.21	1.42
2048	5.24	1.95	5.35	1.54
4096	5.53	1.96	5.42	1.48

Silver Nitrate.

The salt was not recrystallized, but was pulverized and dried thoroughly at 130° for about 12 hours. It was then analyzed and yielded 99.92 per cent. of the theoretical amount of silver chloride.

Table XXXIX.—Molecular Conductivity and Percentage Dissociation.

	35°.		50°.		65°.		
V.	μ_v.	α.	μ_v.	α.	μ_v	α.	μ_v80°.
2	99.18	65.4	124.9	65.2	152.2	65.5	177.7
8	119.5	78.8	150.7	78.7	184.8	79.5	215.4
32	133.5	88.0	168.6	88.0	207.7	89.4	243.4
128	142.6	94.0	180.4	94.2	221.4	95.3	262.0
512	148.3	97.8	187.7	98.0	229.0	98.5	...
1024	150.2	99.0	190.1	99.3	230.7	99.3	...
2048	151.7	100.0	191.5	100.0	232.4	100.0	...

Table XL.—Temperature Coefficients.

	35° to 50°.		50° to 65°.		65° to 80°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	1.71	1.72	1.82	1.46	1.70	1.12
8	2.08	1.74	2.27	1.51	2.04	1.10
32	2.34	1.75	2.61	1.55	2.38	1.15
128	2.52	1.77	2.73	1.51	2.71	1.22
512	2.63	1.77	2.75	1.46	..	..
1024	2.66	1.77	2.71	1.43	..	..
2048	2.65	1.75	2.73	1.43	..	..

Oxalic Acid.

The acid used was recrystallized three times from water. It was then dissolved in water and the strength of this solution was determined by means of potassium hydroxide solution, which had been standardized with sulphuric acid. The latter was estimated as barium sulphate.

The measurement of solutions more dilute than those given in the table was attempted but these were found to be unreliable on account of oxidation brought about by the platinum surface.

Table XLI.—Molecular Conductivity.

V.	μ_v 35°.	μ_v 50°.	μ_v 65°.
4	171.8	194.6	211.1
8	211.6	240.1	262.8
32	291.5	333.9	371.7

Table XLII.—Temperature Coefficients.

	35° to 50°.		50° to 65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
4	1.52	0.885	1.10	0.565
8	1.90	0.898	1.51	0.629
32	2.83	0.971	2.52	0.755

Malonic Acid.

The acid was recrystallized from a mixture of chloroform and acetone, dried in the air, pulverized and then dried in a desiccator. It showed the correct melting point.

Table XLIII.—Molecular Conductivity.

V.	μ_v 35°.	μ_v 50°.	μ_v 65°.
4	31.98	37.38	41.47
16	61.45	71.76	79.73
64	111.8	130.8	145.8
128	148.4	173.8	191.7
512	237.3	277.8	310.9
1024	282.9	331.6	....

Table XLIV.—Temperature Coefficients.

	35° to 50°.		50° to 65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
4	0.360	1.13	0.273	0.730
16	0.687	1.12	0.531	0.740
64	1.27	1.14	1.00	0.765
128	1.69	1.14	1.19	0.685
512	2.70	1.14	2.21	0.796
1024	3.25	1.15	....	....

Succinic Acid.

The substance was purified by recrystallizing twice from water. It was dried in the air, pulverized and then dried in a desiccator.

XLV.—Molecular Conductivity.

V.	μ_v 35°.	μ_v 50°.	μ_v 65°.
8	9.24	11.00	12.40
32	18.52	21.94	24.71
128	36.00	42.64	48.07
512	69.56	82.36	91.17
1024	92.7	109.9	125.4
2048	123.5	145.8	162.7

Table XLVI.—Temperature Coefficients.

	35° to 50°.		50° to 65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
8	0.117	1.27	0.093	0.845
32	0.228	1.23	0.185	0.843
128	0.443	1.23	0.362	0.849
512	0.853	1.23	0.587	0.713
1024	1.15	1.24	1.03	0.937
2048	1.49	1.21	1.13	0.775

Acetic Acid.

The substance was recrystallized twice by cooling. It was then dissolved in water and the strength of the solution determined as in the case of oxalic acid. From the solution of acetic acid of known strength the 0.5 N solutions were prepared by diluting to a definite volume.

Table XLVII.—Molecular Conductivity.

V.	μ_v 35°.	μ_v 50°.	μ_v 65°.
2	2.361	2.720	3.013
8	4.913	5.621	6.240
32	9.79	11.19	12.40
128	19.26	22.04	24.48
512	36.86	41.84	46.31
1024	51.23	58.29	65.2

Table XLVIII.—Temperature Coefficients.

	35° to 50°.		50° to 65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	0.0239	1.01	0.0195	0.717
8	0.0472	0.961	0.0413	0.735
32	0.0933	0.953	0.0807	0.721
128	0.185	0.960	0.163	0.740
512	0.332	0.901	0.298	0.712
1024	0.471	0.919	0.461	0.791

Benzoic Acid.

The substance was purified by recrystallizing twice from water and then dried in a desiccator. It showed the correct melting point.

Table XLIX.—Molecular Conductivity.

V.	μ_v 35°.	μ_v 50°.	μ_v 65°.
64	25.48	29.46	32.21
128	35.44	40.81	45.56
512	67.10	77.63	82.90
1024	89.19	103.4	113.5
2048	117.1	135.6	148.2

Table L.—Temperature Coefficients.

	35° to 50°.		50° to 65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
64	0.265	1.04	0.183	0.621
128	0.358	1.01	0.317	0.777
512	0.702	1.05	0.351	0.452
1024	0.947	1.06	0.673	0.651
2048	1.23	1.05	0.840	0.619

o-*Phthalic Acid.*

The acid was recrystallized twice from water, dried, pulverized and allowed to stand in a desiccator over sulphuric acid.

Table LI.—Molecular Conductivity.

V.	μ_v 35°.	μ_v 50°.	μ_v 65°.
32	71.4	82.1	90.5
64	96.2	110.8	122.8
128	128.2	147.7	163.9
512	213.3	246.9	271.5
1024	258.6	300.3	336.3
2048	301.9	351.5	394.3

Table LII.—Temperature Coefficients.

	35° to 50°.		50° to 65°.	
V.	Cond. units.	Per cent	Cond. units.	Per cent.
32	0.713	0.999	0.560	0.682
64	0.973	1.01	0.800	0.722
128	1.30	1.01	1.08	0.731
512	2.24	1.05	1.64	0.664
1024	2.78	1.07	2.40	0.799
2048	3.31	1.10	2.85	0.811

Salicylic Acid.

The acid was recrystallized twice from water and after drying was pulverized. It was then dried thoroughly in a desiccator over sulphuric acid. It was weighed directly in making the solutions.

Table LIII.—Molecular Conductivity.

V.	μ_v 35°.	μ_v 50°.	μ_v 65°.
64	94.27	111.3	124.8
128	126.1	148.8	166.5
512	210.3	248.0	276.8
1024	253.3	299.0	335.4
2048	294.5	348.8	387.0

Table LIV. Temperature Coefficients.

	35° to 50°.		50° to 65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
64	1.14	1.21	0.900	0.809
128	1.51	1.20	1.18	0.793
512	2.51	1.19	1.92	0.774
1024	3.05	1.20	2.43	0.813
2048	3.62	1.23	2.55	0.731

It was pointed out some time ago[1] that the chief factor in conditioning the increase in the conductivity of electrolytes with rise in temperature is *the increase in the velocities with which the ions move.*

There are a number of factors determining the velocity with which an ion moves through a solution of an electrolyte. Assuming a constant driving force the velocity is conditioned chiefly by the viscosity of the medium surrounding the ion and through which it moves, and by the size and *mass* of the ion. With rise in temperature the driving force would increase, the viscosity of the medium diminish, and both of these factors would increase the velocity with which the ions move.

Another factor of even greater importance as conditioning the effect of temperature on the velocity of the ion is *the change in the mass of the ion with change in temperature, the hydration or solvation of the ion decreasing with rise in temperature.*

The hydrates or solvates surrounding the ions are unstable—the higher the temperature the less complex the hydrate. The smaller the number of molecules of water in combination with the ion, the smaller the mass of the ion, and the less its resistance in moving through the solvent. Consequently, rise in temperature will cause the ion to move faster through the solvent.

If the factor of diminishing complexity of the hydrate with rise in temperature plays a prominent part in determining the large temperature coefficient of conductivity, we should be able to establish relations at the higher analogous to those at the lower temperatures.

We shall now see whether the relations between temperature coefficients of conductivity and hydration that were found to hold between 0° and 35° hold also between 35° and 65°.

From the following tables the sulphates are omitted, both those that crystallize with much water and are, therefore, largely hydrated in solution, and those that crystallize with only a small amount of water and whose solutions represent only slight hydration. This is done because the sulphates

[1] THIS JOURNAL, **35**, 445 (1906).

are largely polymerized in aqueous solutions, and, therefore present irregularities to any relation that can be pointed out.

Table LV.—Substances with Small Hydrating Power.

	Temperature coefficients in conductivity units.			
	35° to 50°.		50° to 65°.	
	$V = 2$.	$V = 2048$.	$V = 2$.	$V = 2048$.
Sodium chloride	1.87	2.69	1.95	2.92
Sodium bromide	1.66	2.65	2.10	3.00
Sodium nitrate	1.67	2.53	1.73	2.53
Potassium chloride	2.15	2.97	2.12	3.15
Potassium bromide	2.13	3.02	2.11	3.13
Potassium nitrate	1.87	2.77	1.91	2.91
Potassium acetate	1.83	2.41	1.88	2.94
Ammonium chloride	2.15	3.09	2.17	3.14
Ammonium nitrate	1.96	2.81	2.06	3.09
Lithium chloride	1.69	2.49	1.76	2.74
Silver nitrate	1.71	2.65	1.82	2.73

Table LVI.—Substances with Large Hydrating Power.

	Temperature coefficients in conductivity units.			
	35° to 50°.		50° to 65°.	
	$V = 2$.	$V = 2048$.	$V = 2$.	$V = 2048$.
Barium chloride	2.95	5.77	2.61	5.53
Barium nitrate	...	5.27	...	5.91
Magnesium nitrate	2.61	5.23	2.74	5.76

The more complex the hydrate, *i. e.*, the greater the number of molecules of water combined with an ion, the greater the *change in the complexity of the hydrate with rise in temperature.*

We should therefore expect to find that *those ions with the largest hydrating power have the largest temperature coefficients of conductivity.*

If we compare the results in Table LVI with those in Table LV we shall find the above conclusion very beautifully confirmed by the facts. The substances in Table LVI have large, those in Table LV relatively small hydrating power. The comparisons are made at volumes 2 and 2048—fairly concentrated and fairly dilute solutions. They are also made over the ranges of temperature 35°–50° and 50°–65°.

A glance at the two tables will show that the temperature coefficients in Table LV are much smaller than those in Table LVI for the same concentrations and temperatures, even taking into account the fact that the substances in Table LVI are ternary, while those in Table LV are binary electrolytes.

If the temperature coefficient of conductivity is chiefly a function of the complexity of the hydrate formed by the ions, then *those substances that have approximately equal hydrating power should have approximately the same temperature coefficients of conductivity.* An examination of the two tables will show that this relation holds. The substances in Table LV all have very small hydrating power, which in general is of the same order of magnitude. It will be seen that the temperature coefficients both for $V = 2$ and $V = 2048$ are of the same order of magnitude at both the lower and the higher temperatures.

In Table LVI a similar relation manifests itself. The temperature coefficients for these substances are of the same order of magnitude at the different volumes and over the two ranges of temperature. These substances all show hydration of the same order of magnitude.

One other relation of importance comes out from a study of the above tables. The complexity of the hydrates at the higher dilution is greater than at the lower—the complexity increasing in general with the dilution, as has been shown by work done in this laboratory. The hydrate being more complex at the higher dilution, the change in the complexity of the hydrate with change in temperature would be greater at the higher dilution and, consequently, the temperature coefficient of conductivity would be greater the more dilute the solution.

An examination of the tables will show that *at the higher dilution the temperature coefficient of conductivity for any given substance is greater than at the lower dilution.*

We can summarize the results thus far obtained between 35° and 65° in exactly the same way as those obtained between 0° and 35°.[1]

[1] THIS JOURNAL, **35**, 450 (1906).

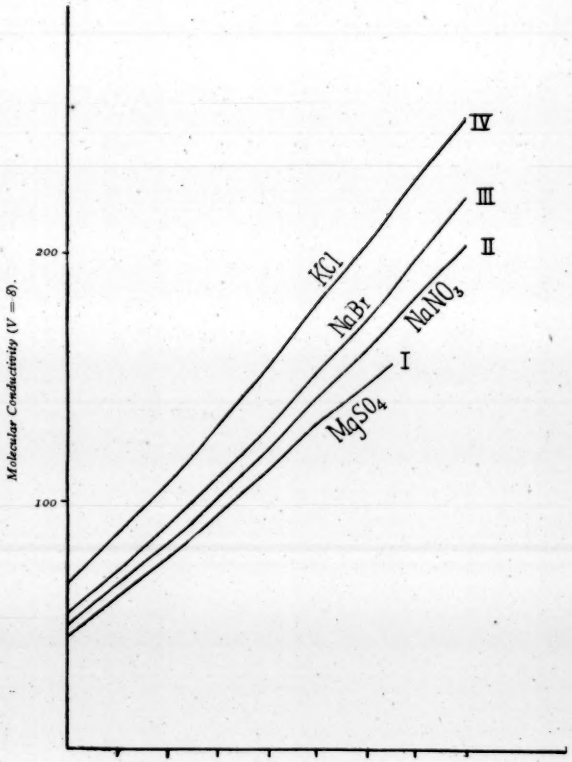

IV
III
II
I
KCl
NaBr
NaNO3
MgSO4
200
100
Molecular Conductivity (V = 8).
10
20
30
40
50
60
70
80
Temperature.

Fig. 1.

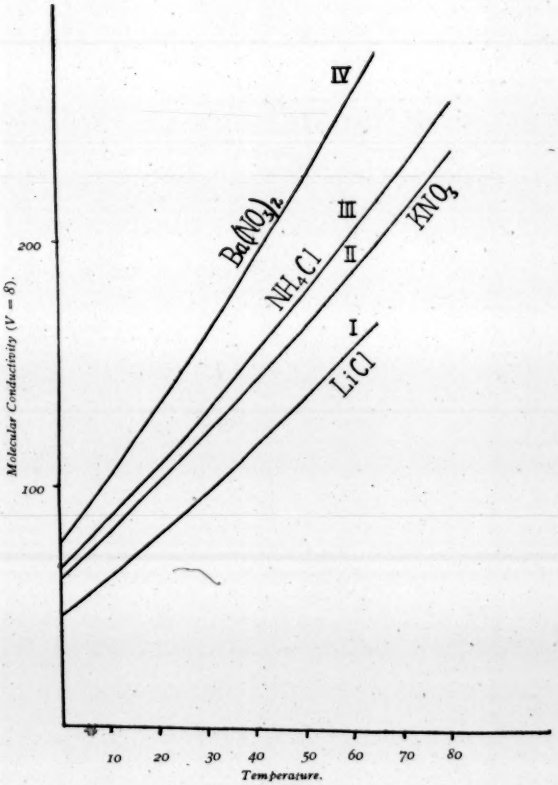

IV
III
II
I
$Ba(NO_3)_2$
NH_4Cl
KNO_3
LiCl
200
100
Molecular Conductivity (V = 8).
10
20
30
40
50
60
70
80
Temperature.

Fig. 2.

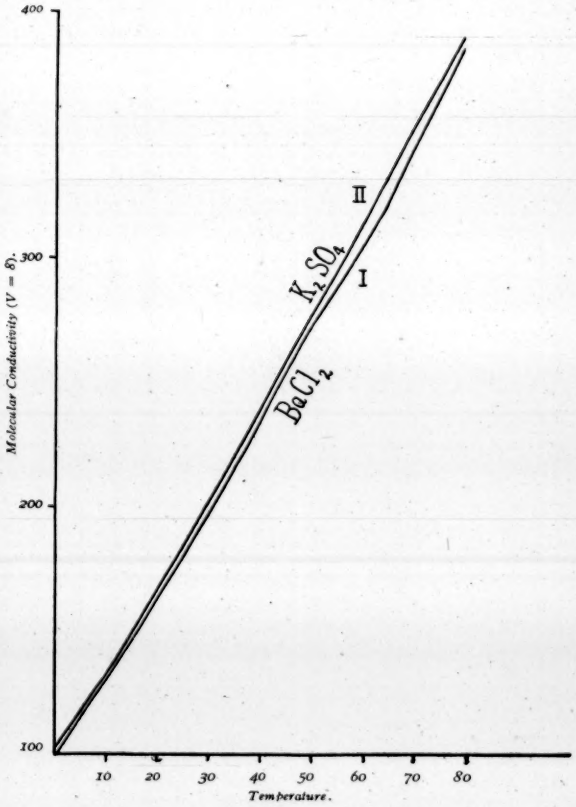

400
300
200
100
Molecular Conductivity (V = 8).
10
20
30
40
50
60
70
80
Temperature.
II
I
K_2SO_4
$BaCl_2$

Fig. 3.

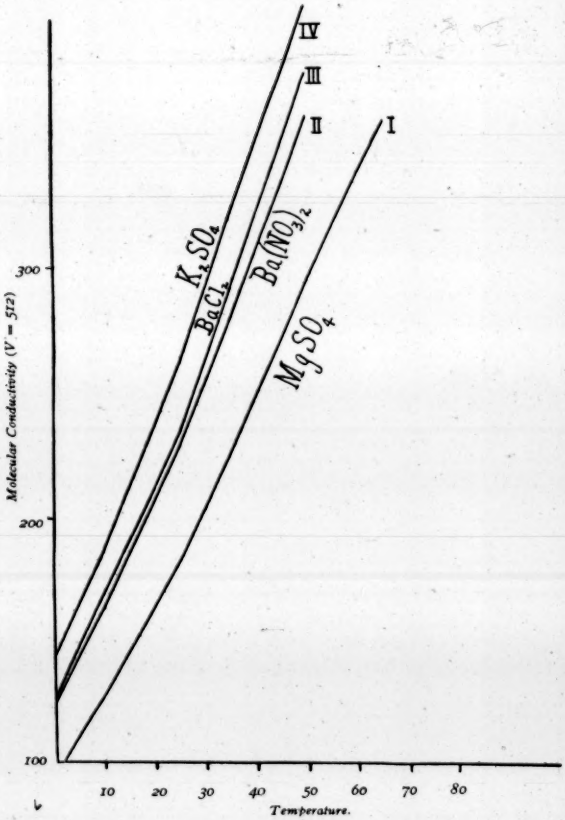

IV
III
II
I
K_2SO_4
$BaCl_2$
$Ba(NO_3)_2$
$MgSO_4$
300
200
100
Molecular Conductivity (V = 512)
10
20
30
40
50
60
70
80
Temperature.

Fig. 4.

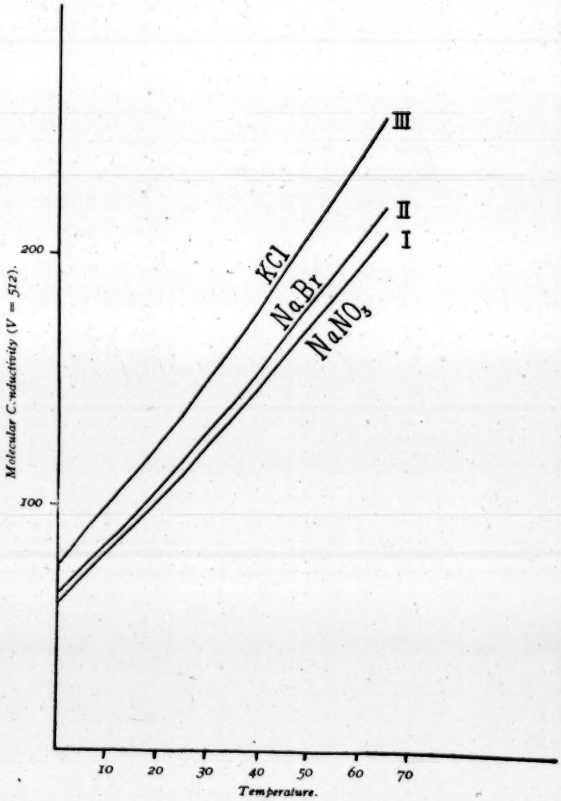

III
II
I
KCl
NaBr
NaNO3
200
100
Molecular Conductivity (V = 512).
10
20
30
40
50
60
70
Temperature.

Fig. 5.

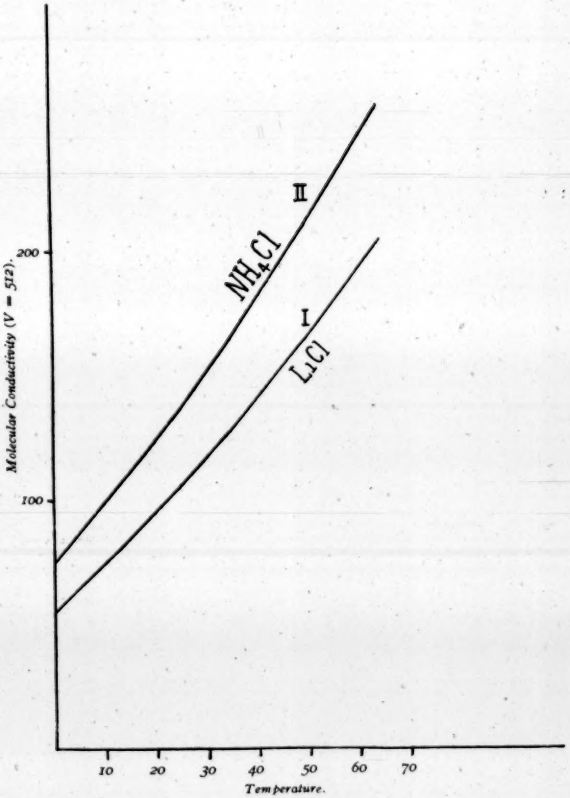

Molecular Conductivity (V = 512).
200
100
NH4Cl
II
I
LiCl
10
20
30
40
50
60
70
Temperature.

Fig. 6.

1. The temperature coefficients of conductivity of aqueous solutions of electrolytes between 35° and 65° are greater, the more complex the hydrates formed by the electrolyte.

2. The temperature coefficients of conductivity of aqueous solutions of electrolytes between 35° and 65° are of the same order of magnitude for those substances having approximately the same hydrating power.

3. The temperature coefficients of conductivity for any given substance increase with the dilution of the solution and the increase is greatest for the substances with the largest hydrating power.

It should be noted that all three of the above conclusions follow of necessity from the assumption that the change in conductivity with change in temperature is due largely to the decreasing complexity of the hydrates formed around the ions as the temperature is raised.

The results for a number of compounds are plotted as curves, the molecular conductivities being ordinates and the abscissas temperature. The curves do not differ greatly from straight lines.

It will be noted that there is a general tendency in the dissociation to decrease slightly with rise in temperature.

Not very much work was done at 80° on account of possible changes in the cell constant, the solubility of the glass, and other sources of error that are liable to come in at the higher temperature.

We are extending this work, which has now been in progress in this laboratory for nine years, to all of the more common electrolytes, inorganic and organic, between 35° and 65°.

PHYSICAL CHEMICAL LABORATORY,
JOHNS HOPKINS UNIV.,
JUNE, 1909.

THE ABSORPTION SPECTRA OF SOLUTIONS; A POSSIBLE METHOD FOR DETECTING THE PRESENCE OF INTERMEDIATE COMPOUNDS IN CHEMICAL REACTIONS.

By Harry C. Jones and W. W. Strong.

(The following results were obtained in an investigation that is being carried out with the aid of a Grant from the Carnegie Institution of Washington.)

Jones and Anderson[1] have shown that neodymium chloride has very different absorption bands in water and in alcohol, and Jones and Strong[2] have found a large number of examples illustrating the effect of the solvent on the absorption of light by the dissolved substance. A number of uranous and uranyl salts show different bands in each of the following solvents: water, methyl and ethyl alcohols, glycerol and acetone.

These facts, as has been pointed out, are good evidence for the theory of solvation in terms of which we have been working in this laboratory for a number of years.

It is difficult, not to say impossible, to see how a nonabsorbing solvent can affect the absorption of the dissolved substances unless it enters into some kind of combination with them.

Another set of facts has recently come to light which makes it highly probable that the property of solutions to absorb light can be utilized to detect the presence of intermediate compounds in chemical reactions. Our chemical equations would teach us that when a salt AB is treated with a small amount of a strong acid C, most of the compound AB remains, and a small amount of AC is formed. As the amount of the acid C is increased, the amount of AC increases, until finally we have practically only the compound AC and the free acid B.

Chemists have, however, long suspected that chemical reactions are much more complex than is usually represented

[1] This Journal, **41**, 163. Carnegie Institution of Washington, Publication No. 110.

[2] This Journal, **43**, 37, 99 (1910).

by our chemical equations. The existence of a number of intermediate products between the initial and final substances seems highly probable. The study of reaction velocities in terms of the law of mass action has shown that many reactions that were regarded as direct and simple are in reality composed of a number of more or less independent reactions. The products of such reactions must, therefore, be much more complex than is usually represented by our equations. The intermediate products formed in such reactions have, in most cases, not been isolated. This is often due to their instability, and also to the lack of sufficiently refined methods for dealing with such problems.

Our work on the power of solutions to absorb light has made it highly probable that intermediate compounds exist in reactions, at least those in which uranium salts are involved.

An aqueous solution of uranyl nitrate has a perfectly definite absorption spectrum. An aqueous solution of uranyl sulphate has likewise a perfectly definite spectrum. If we were to add a small amount of sulphuric acid to a solution of uranyl nitrate and then photograph the absorption spectrum, we would expect to find the bands corresponding to the nitrate coming out strongly, and, simultaneously, those corresponding to the sulphate coming out faintly, since there would be much nitrate and only a little sulphate present. As the amount of sulphuric acid is increased we would expect to find the nitrate bands becoming fainter and fainter and the sulphate bands stronger and stronger, until we should have only the sulphate bands present when practically all of the nitrate had been transformed into sulphate.

The facts are not in accord with these predictions. When sulphuric acid is added to a solution of uranyl nitrate containing free nitric acid (to make the bands sharper) we do not get the absorpton spectrum characteristic either of the nitrate or of the sulphate, but we get a spectrum that is intermediate between the two. Certain of the bands which appeared in the nitrate spectrum are shifted to new positions, the amounts of the shifts depending on the amounts of sulphuric

acid added. As the sulphuric acid present is increased these bands continue to shift until they occupy the positions of the bands of the pure sulphate to which free sulphuric acid had been added.

Even more striking results of the above character were obtained when hydrochloric acid was added to an aqueous solution of uranyl nitrate containing free nitric acid. As the amount of the hydrochloric acid was increased certain of the nitrate bands were greatly shifted, and finally occupied the positions of certain of the chloride bands.

Uranyl nitrate treated with hydrobromic acid behaves in the same manner as when treated with hydrochloric acid.

The most striking example of the above effect, as far as our observations have gone, is the action of nitric acid on an aqueous solution of uranous acetate containing free acetic acid. The addition of more and more nitric acid caused the uranous bands to disappear as the uranous salt passed over into the uranyl condition. At the same time two pairs of the uranyl acetate bands *gradually shifted* their positions and finally united, forming single nitrate bands.

These results are not at all in keeping with the predictions from our chemical conceptions of what takes place in such reactions. The *gradual shift of the bands* when sulphuric acid is added to a solution of uranyl nitrate would indicate the possibility of the formation of a series of more or less unstable systems or compounds, intermedia tein composition between the nitrate and the sulphate. Similarly, when hydrochloric acid is added to an aqueous solution of uranyl nitrate the gradual shift in the bands would indicate that a series of systems or compounds, is formed, the composition depending upon the amount of hydrochloric acid present.

A similar interpretation of the results obtained when nitric acid is added to an aqueous solution of uranous acetate appears to be necessary.

These results from absorption spectra seem to show that in such reactions, at least in those referred to above, we do not have the final product formed at once from the initial substances, as our chemical equations would indicate, but that a

series of more or less unstable intermediate compounds is formed.

It is impossible to say at present of how wide applicability the absorption spectra method is as a means of detecting the presence of intermediate compounds in chemical reactions. For this method to be applicable it is necessary that the solutions of the different salts taking part in the reaction should have different absorption bands, but a number of salts fulfil this condition.

It is now a matter of interest to isolate these intermediate compounds wherever possible, since their existence in solution seems to be indicated by their absorption spectra.

Further work along these lines will be carried out in this laboratory.[1]

PHYSICAL CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
JANUARY, 1910.

[Contribution from the Kent Chemical Laboratory of the University of Chicago.]

ON THE BEHAVIOR OF THE ORDINARY HEXOSES TOWARDS HYDROGEN PEROXIDE IN THE PRESENCE OF ALKALINE HYDROXIDES, AS WELL AS OF VARIOUS IRON SALTS.

BY H. A. SPOEHR.

The experiments of Nef and his students[2] prove that the various hexose sugars are split in alkaline solution, through formation of 2,3- and 3,4-dienols, into diose, and isomeric trioses and tetroses, which, in the form of dienols, can also

[1] Since the above note was sent to press the following results have been obtained with salts of neodymium. The different salts of neodymium show, in general, very much the same absorption bands. The absorption spectrum of an aqueous solution of neodymium acetate, however, differs very considerably from that of the chloride, the nitrate or the sulphate.

Spectrograms have therefore been made, showing the changes that take place when different amounts of hydrochloric or nitric acid are added to neodymium acetate. The results were of the same general character as with the uranyl salts. While nitric acid made the bands broad and hazy, hydrochloric acid produced a number of new bands intermediate in position between those of the acetate and the chloride. We interpret these results as we interpreted those with the uranyl salts. A number of intermediate systems or compounds between the acetate and the chloride are formed.

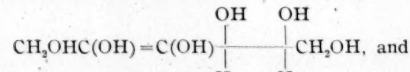
[2] Ann. Chem. (Liebig), **357**, 214–312. Anderson: THIS JOURNAL, **42**, 401–430.

give, by further dissociation, hydroxymethylene or formaldehyde molecules.[1] We know further through the work of Lobry de Bruyn and Ekenstein[2] on *d*-galactose and *d*-glucose, respectively, that certain isomeric aldo- and 2-ketohexoses are reciprocally interconvertible in alkaline solution. Nef has shown[3] that this must be due to an intermediate formation of 1,2-dienols, which can then add water in various ways to give the isomeric sugars actually obtained; he concluded further,[4] from theoretical considerations, that glutose and galtose, obtained by Lobry de Bruyn and Ekenstein[5] from *d*-glucose and *d*-galactose by means of calcium as well as lead hydroxide, must each consist of a mixture of two isomeric 3-ketohexoses, to which he therefore gave the names α- and β-*d*-glutose and α- and β-*d*-galtose, respectively. My work (see below) proves the correctness of the conclusion of Nef with reference to the constitution and nature of the sugars last named, so that it is now certain that glutose and galtose are isomeric 3-ketohexose sugars of the dextro series. Furthermore, since the *d*-glutose and *d*-galtose sugars are not mutually interconvertible by means of caustic alkalies and also never give the corresponding members of the laevo series under the conditions named, Nef[6] concluded that the 3-ketohexoses must give 2,3-dienols by preference and, further, that the moment 3,4-dienol formation takes place, a spontaneous splitting into two molecules of glyceric aldehyde must result. He concluded finally also that the conversion of aldo- and 2-ketohexoses into the isomeric 3-ketohexoses was a nonreversible process,[7] and explained this on the assumption that the 2,3-dienols must add water so as to give 3-ketohexoses only:

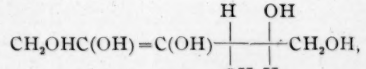
$$CH_2OHC(OH)=C(OH)CHOHCHOHCH_2OH + HOH \longrightarrow$$
$$CH_2OHCHOHC(OH)_2CHOHCHOHCH_2OH \longrightarrow$$
$$CH_2OHCHOHC(=O)CHOHCHOHCH_2OH + H_2O.$$

[1] Ann. Chem. (Liebig), **335**, 195, 282.
[2] Rec. Trav. Chim., **14**, 158, 203; **15**, 92; **16**, 257; **19**, 1.
[3] Ann. Chem. (Liebig), **357**, 294.
[4] *Ibid.*, **357**, 297.
[5] Rec. Trav. Chim., **16**, 258, 269, 274.
[6] Ann. Chem. (Liebig), **357**, 299.
[7] *Ibid.*, **357**, 297.

Dr. Nef tells me that he now considers this conclusion, which was based entirely upon the work of the Dutch chemists named above—namely, that glutose and galtose cannot be converted back into 2-keto and aldohexose sugars by alkalies—very improbable. It seems to him that the only rational way in which to explain the reciprocal transformation (by alkaline hydroxides) of *d*-fructose and pseudofructose, on the one hand, and of *d*-tagatose and *l*-sorbose, on the other hand, is on the basis that the 2,3-dienol common to the 2- and 3-ketohexoses under consideration,



2,3-Dienol common to *d*-fructose, pseudofructose and α- and β-*d*-glutose.



2,3-Dienol common to *d*-tagatose, *l*-sorbose, and α- and β-*d*-galtose.

must add water to the ethylene grouping so as to give *all* the isomeric 2- and 3-ketohexoses under consideration; this naturally means, therefore, that the 3-ketohexoses must go back in the presence of alkaline hydroxides (aside from their splitting into diose, triose and tetrose mentioned above) into 2-keto- and aldohexose sugars of the *corresponding* dextro series; it is, however, exceedingly probable tbat these last named sugars (in all, six of one series) are finally present in relatively far smaller amounts than the main components—the two isomeric 3-ketohexose sugars. This would explain why Lobry de Bruyn and Ekenstein were never able to prove that glutose or galtose go back with alkalies into 2-keto- and aldohexoses; it would, in fact, be impossible to establish this experimentally by any methods yet known.

Turning now to the final explanation of the action of Fehling's solution on sugars, as given by Nef in the recent thesis

of Anderson,[1] it will at once be seen how beautifully this is in harmony with the conclusions just presented. *d*-Mannose, *d*-glucose, and *d*-fructose all give the same oxidation products in the presence of sodium and cupric hydroxides, namely, carbon dioxide, formic, glycollic, *d,l*-glycerinic acid, *l*-threonic and *d*-erythronic lactones (trihydroxybutyric acids) and the three hexonic acids—*d*-mannonic, *d*-gluconic and α-hydroxymethyl-*d*-arabonic acid. The formic acid obviously comes from the oxidation of the hydroxymethylene molecules, whereas the diose, triose and *d*-erythrose (present as dissociation products of the 2,3- and 3,4-dienols of the hexoses under consideration) as well as the aldo-, 2- and 3-ketohexoses at first present or subsequently formed in the alkaline solution, are oxidized to their corresponding osones, and then give by a benzilic acid rearrangement (asymmetric in part or entirely) the various acids just named.

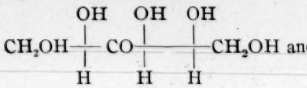
When *d*-galactose (or *d*-tagatose or *d*-talose) are oxidized with Fehling's solution the same products and in approximately the same ratio are obtained as with the members of the *d*-glucose series, excepting that in place of the three hexonic acids mentioned above we now obviously obtain *d*-galactonic, *d*-talonic (from 1,2-galactosone), and α-hydroxymethyl-*d*-lyxonic acid (from the 2,3-galtosone) by an asymmetric benzilic acid rearrangement.

Since preliminary experiments by Dr. Nef and his students[2] with hexoses had shown that these sugars, when oxidized in the presence of sodium, potassium, barium or calcium hydroxide by air, or freshly precipitated oxide of mercury, give practically the same oxidation products and in the same ratio as with Fehling's solution, I began experiments, at Dr. Nef's suggestion and under his guidance, on the oxidation of *d*-glucose and *d*-galactose in alkaline solutions in the presence of hydrogen peroxide. It was at first expected, especially also because of the preliminary observations published by Buchner, Meisenheimer and Schade,[3] that besides much formic acid the same hydroxy acids would be obtained as when air, oxide

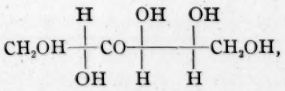
[1] THIS JOURNAL, **42**, 403.
[2] *Ibid.*, **42**, footnote, p. 406.
[3] Ber. d. chem. Ges., **39**, 4217; **41**, 1009, footnote.

of mercury, or copper, was present besides the caustic alkali. There was, however, this remarkable difference: *d*-glucose and *d*-fructose each gave only four oxidation products, namely, small amounts of carbon dioxide, glycollic, and α-hydroxymethyl-*d*-arabonic acids; and the main reaction product was formic acid, 48.3 to 65.3 per cent. of the calculated possible amount. With *d*-galactose still smaller amounts of the three corresponding acids, carbonic, glycollic and α-hydroxymethyl-*d*-lyxonic acids, were obtained; in this case over 80 per cent. of the sugar was oxidized to formic acid! We have here, therefore, remarkable instances of what is temporarily called selective oxidation. As stated above, an alkaline solution of *d*-glucose slowly gives the following 8 hexose sugars: *d*-glucose, *d*-mannose, *d*-fructose, α- and β-*d*-glutose, *d*-allose, *d*-latose, and *d*-pseudofructose; the solution contains in addition, through spontaneous dissociation of the 2,3- and 3,4-dienols of these hexoses, formaldehyde, diose, triose, and tetrose sugars. The situation in the case of *d*-galactose is entirely similar except that we must substitute the eight members of the *d*-galactose series, *i. e.*, certain aldo- and 2- and 3-keto-hexoses[1] for those members of the *d*-glucose series just named.

In the presence of the hydrogen peroxide, therefore, the only sugars present in the alkaline solution which are actually selectively oxidized are: (1) formaldehyde, hydroxymethylene, which can be present only in marvellously small concentration, and yet is the source of all the formic acid actually obtained; (2) glycollic aldehyde, which is transformed in part into glycollic acid and in part through an intermediate formation of glyoxylic acid into carbon dioxide and formic acid; (3) α- and β-*d*-glutose,

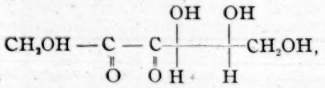


and

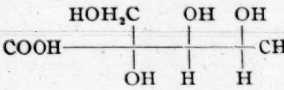


[1] Nef: Ann. Chem. (Liebig), **357**, 295.

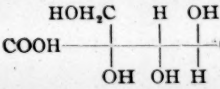
which give the same 2,3-glutosone,



and this by an *entire* asymmetric benzilic acid rearrangement[1] then gives *only* α-hydroxymethyl-*d*-arabonic acid,



formed from *d*-galactose give, by an entirely analogous reaction, α-hydroxymethyl-*d*-lyxonic acid,



tioned.

The first case of selective oxidation of sugars observed in this laboratory was by Miss Denis.[2] She found that acetol, when oxidized in alkaline solution in the presence of mercuric oxide, gives practically *d,l*-lactic acid only, whereas, when silver oxide is present besides the caustic alkali, acetic and formic acids are the only oxidation products obtained. Now it is clear from Nef's work that an alkaline solution of acetol (= methyldiose) contains the following substances: acetol, CH_3—CO—CH_2OH, and its dienol, CH_3COH=$CHOH$; acetylmethylene, CH_3CO—$CH\rightleftarrows$ + H_2O $\rightleftarrows$ CH_3—CO—CH_2OH; hydroxymethylene, $\rightleftarrows CHOH$, and hydroxyethylidene, $CH_3COH\rightleftarrows$ —the dissociation products of the 1,2-dienol of acetol. In the case of silver oxide, the last two named substances are therefore obviously the only two products oxidized, whereas with the oxide of mercury, the acetylmethylene molecules are selectively chosen and converted into pyruvic aldehyde by oxidation, and this is then at once transformed by a benzilic acid rearrangement into *d,l*-lactic acid.

[1] Nef: Ann. Chem. (Liebig), **298**, 305.
[2] This Journal, **38**, 579.

EXPERIMENTAL PART.

Part I. Behavior of d-*Glucose,* d-*Fructose and* d-*Galactose towards Alkaline Hydrogen Peroxide.*

a. Quantitative Determination of the Amounts of Carbon Dioxide and of Formic Acid Formed in the Oxidation.—Two grams of sugar were dissolved in 80 cc. of three per cent. solution of hydrogen peroxide[1] (6.5 molecules); no action was ever observed to take place under these conditions even on long standing. The colorless mixture was at once poured into a solution of 5.62 grams potassium hydroxide (9 molecules) in 100 cc. water, and diluted with water so that the initial concentration of the alkali was approximately half normal; the presence of a soda-lime tube prevented the access of carbon dioxide from the air and permitted the escape of hydrogen. The solution always remained absolutely colorless—in marked contrast to the strong coloration noticed when sugar solutions are allowed to stand alone with soluble alkaline hydroxides; there was no appreciable rise in temperature, but a noticeable difference in the speed of oxidation of *d*-fructose, *d*-glucose and *d*-galactose was observed—the reaction, proceeding most rapidly with the last named sugar, and far more slowly with *d*-glucose. This must finally be the sole basis for explaining (especially in the case of *d*-glucose and *d*-fructose) the remarkable differences in the relative amounts of the four oxidation products observed. It is therefore probable that a difference in the ratio of the four oxidation products formed would also be observed by simply varying the concentrations in the oxidation of the same sugar, but I have not as yet carried out any experiments to test this point. After allowing the above-mentioned solution to stand for two days in the case of *d*-galactose, and for three days in the case of the two other sugars named, no more sugar was found present, as shown by testing with Fehling's solution; the excess of hydrogen peroxide was then destroyed by adding a little platinum black and stirring violently. The amount of carbon dioxide, as well as of formic acid, formed in the oxida-

[1] The exact strength of this reagent was always determined just before using by titration with permanganate. Cf. Classen: Quant. Anal., II, 211.

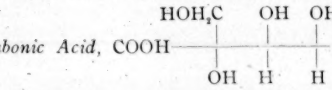
tion, was then determined as follows: the calculated amount of aqueous hydrogen chloride was first added, by means of a separatory funnel, to the alkaline solution in a flask, which was connected with a reflux condenser and a series of cylinders containing saturated solutions of barium hydroxide. Air free from carbon dioxide was continually drawn through the acidified solution and finally the flask was heated in a bath kept between 110°–120° for one hour, to ensure the complete expulsion of carbon dioxide. The barium carbonate precipitated in the cylinder was well washed, dried at 100°, and then weighed. A correction was, of course, made for the amount of carbon dioxide present in the potassium hydroxide used, as determined by a blank experiment. In order to determine the formic acid remaining in the aqueous solution, it was removed, together with the water, by distilling under 15–30 mm. pressure from a flask provided with a Kjeldahl bulb to prevent volatilization of glycollic acid, heating finally on a boiling water bath, and then redissolving the residue in a small amount of water and repeating the distillation. The aqueous distillates proved to be free from traces of hydrogen chloride and were then made up to a definite volume; the amount of the formic acid present in an aliquot portion was then determined by titration with 0.1 N alkali as well as by oxidation to carbon dioxide with 0.1 N permanganate.[1] Since the two methods gave results which agreed perfectly, it is certain that no acid other than formic acid could have been present. Oxalic acid was also looked for with especial care in the non-volatile salt residue, but always with negative results. Herewith is given a summary of the quantitative results obtained in the oxidation of the three sugars named:

2 grams of *d*-fructose gave 0.105 gram CO_2, *i. e.*, 3.58 per cent.; and 1.48 grams formic acid, *i. e.*, 48.3 per cent. of the amount theoretically possible.

2 grams of *d*-glucose gave 0.103 gram CO_2, *i. e.*, 3.51 per cent.; and 2.00 grams formic acid, *i. e.*, 65.3 per cent.

2 grams of *d*-galactose gave 0.143 gram CO_2, *i. e.*, 4.65 per cent.; and 2.46 grams formic acid, *i. e.*, 80.2 per cent.

[1] H. C. Jones: THIS JOURNAL, **17**, 539.

*b. The Nonvolatile Acids, Glycollic and α-Hydroxymethyl-*d-*arabonic Acid,*  *from* d-*Fructose and* d-*Glucose.*—In order to determine the nature of the nonvolatile acids left with the salt residue after the removal of the water and volatile acids by distillation, as stated above, at least 100 grams of sugar had to be taken for oxidation (usually in four operations with 25 grams). The reactions had invariably proceeded to completion after standing three days at ordinary temperature, and it was now found more convenient to get rid of the hydrogen peroxid still present by longer standing or more rapidly by simply heating for a short time. It was furthermore also found advisable to add subsequently a slight excess over the calculated amount of hydrogen chloride, and then to remove the water and volatile acids, including also a part of the excess of hydrogen chloride, by distilling at 15–30 mm. as before, heating finally on a boiling water bath; if only the calculated amount of hydrogen chloride is added some potassium glycollate, melting at 149°, and supposed at first to be *d*-mannonic lactone, is always obtained after extracting the salt residue thoroughly with absolute alcohol and subsequent concentration of the alcoholic filtrates. I obtained, for example, by proceeding in this way with 100 grams *d*-fructose, a total of 19.42 grams of potassium glycollate (in four crops) melting at 147°–149° and crystallizing in glistening needles. These gave, on treatment with an excess of hydrogen chloride, etc., and subsequent extraction of the salt residue with ether, 13.2 grams of crude glycollic acid melting from 72°–74°. Its identity with glycollic acid was proved, first, by titration with 0.1 N potassium hydroxide: 0.3534 gram in 50 cc. water required for neutralization 45.4 cc. 0.1 N potassium hydroxide; second, by conversion into the phenylhydrazine salt, described by Nef:[1] 0.4 gram in 1 cc. alcohol and 0.5 gram phenylhydrazine yielded 0.7 gram of the glistening white plates melting at

[1] Ann. Chem. (Liebig), **357**, 223.

100°; and third, by transformation into the characteristic calcium salt.

The original alcoholic filtrate from the 19.42 grams of potassium glycollate mentioned above was found, after removal of the alcohol by distillation under diminished pressure, to contain a large amount of gum which was first treated with a small amount of hydrogen chloride, etc., and then separated from a small amount of chloride of potassium by dissolving in a little absolute alcohol. The clear light brown gum finally obtained weighed 20 grams and was then resolved by digestion with ether and with acetic ether: (1) Into a portion, A, soluble in ether, 3.4 grams; (2) into a portion, B, soluble in much acetic ether, 12.93 grams; and (3) into an insoluble portion, C, 3.47 grams, which still contained some tar and potassium chloride, since on acylation with 11 cc. acetic anhydride, and subsequent hydrolysis of the acylated material soluble in ether, only 2.31 grams of gum were recovered. Gum A, treated with an excess of powdered strychnine, etc., gave a total of 12.9 grams of crude glycollic strychnine,[1] melting at 180°–190° and decomposing at 235°, from which 8.25 grams of crystallized calcium glycollate,

$$Ca(C_2H_3O_3)_2.4H_2O,$$

corresponding to 2.4 grams of glycollic acid, were finally obtained. Gum B, after titration of a small portion with tenth-normal alkali, which gave results agreeing with those calculated for trihydroxybutyric lactone, was shown, by conversion of the main portion into brucine salts, to consist only of a mixture of glycollic acid and a new hexonic acid, α-hydroxymethyl-*d*-arabonic acid, According to unpublished observations of Nef, brucine glycollate contains crystal water, melts at 82° (or after loss of crystal water at 120°), and is very soluble in cold absolute alcohol; the brucine salt of the new hexonic acid, on the other hand, melts, according as it contains or loses its crystal water, within the range of 168°–188°, is sparingly soluble in cold absolute alcohol, and separates out from this solvent in the anhydrous form in opaque nodules looking much like brucine *d*-gluconate, and melting at 187°–

[1] Ann. Chem. (Liebig), **357**, 238.

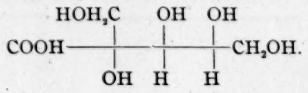
188°. When crystallized from 3 parts of alcohol and one-third part of water, the salt separated out in transparent flat plates melting from 167°–170°; these lose, on drying for a week over sulphuric acid *in vacuo*, a small and indefinite amount of water, but by this process the melting point invariably is raised to 186°–188°. The salt can also be crystallized from a small amount of water. By fractional crystallization of the brucine salts obtained from the gums B and C, separation of these into high (above 160°) and low (120°–140°) melting, and gummy salts, conversion of the gummy and low melting salts into the free acids, and subsequently into the corresponding strychnine salts, and then separation of the difficultly soluble strychnine glycollate from the easily soluble strychnine salt of α-hydroxymethyl-*d*-arabonic acid by crystallization from alcohol, I finally obtained in all from gums A, B and C, 34.7 grams of pure anhydrous brucine α-hydroxymethyl-*d*-arabonate melting from 185°–188°, with $[\alpha]_D^{20} = -25°.94$; this corresponds to 10.34 grams of α-hydroxymethyl-*d*-arabonic lactone. The total amount of glycollic acid obtained from these fractions was only 3.5 grams, which, with the 13.2 grams previously obtained from the potassium salt, makes a total of 16.7 grams of this acid from 100 grams *d*-fructose.

c. d-*Glucose.*—Dextrose and laevulose each give the same four acids by oxidation under the conditions named, but there is a very remarkable difference in the relative amount of these products formed which can be due only to a difference in the speed of oxidation in the two cases, the oxidation proceeding, under the same conditions of concentration, noticeably faster in the case of *d*-fructose. Four portions of twenty-five grams *d*-glucose, melting at 148°–149°, were dissolved each in 865 cc. 3 per cent. hydrogen peroxide (5.5 molecules) and poured into a normal solution of potassium hydroxide containing 70 grams of the alkali (9 molecules), as described above. No sugar was left after standing 65 hours, and on getting rid of the oxidizing agent, adding an excess of hydrogen chloride, etc., an acetic ether extract containing 25.87 grams nonvolatile acids was finally obtained. These were

resolved by two-fold fractional crystallization of the brucine and strychnine salts, as described above under *d*-fructose, into 23.07 grams practically pure glycollic strychnine, corresponding to 4.3 grams free glycollic acid, and into 62.1 grams pure α-hydroxymethyl-*d*-arabonic brucine melting at 183°–188° with $[\alpha]_D^{20} = -25°.7$, corresponding to 18.78 grams of α-hydroxymethyl-*d*-arabonic lactone. This result proves in a most decisive manner that only these two acids could possibly have been present. Especially worthy of notice is the fact that here, in marked contrast to the experiments with *d*-fructose, the amount of glycollic acid formed is exceedingly small; furthermore, *d*-glucose, although its transformation into α- and β-*d*-glutose involves an intermediate formation of lævulose, actually gives a somewhat larger yield of α-hydroxymethyl-*d*-arabonic lactone than does *d*-fructose itself.

In order, therefore, to obtain a sufficiently large amount of the new hexonic acid for an exhaustive study, and especially for the determination of its constitution, a second series of oxidation experiments with eight portions of 25 grams of *d*-glucose (*i. e.*, with 200 grams sugar in all) was carried out under practically the same conditions as those just described. The nonvolatile acids were resolved into an ether extract, 9.7 grams gum, which consisted mainly of glycollic acid, and into an acetic ether extract containing 44.5 grams gum. The latter, after long digestion in aqueous solution with an excess of powdered calcium carbonate and finally with a small amount of powdered quicklime (to ensure complete transformation of the lactone into the salt), gave, on concentration of the aqueous solution, 37.3 grams of the very characteristic calcium α-hydroxymethyl-*d*-arabonate, $Ca(C_6H_{10}O_7)_2.5H_2O$; a large portion of this was used in the oxidation experiment with nitric acid (described below).

*On the Properties and Constitution of the New Hexonic Acid Called α-Hydroxymethyl-*d*-arabonic Acid,*



Brucine Salt.—The homogeneous nature of the acid called α-hydroxymethyl-*d*-arabonic acid was established by a careful study of its crystalline derivatives. The most characteristic of these is perhaps its brucine salt, which separates out very completely on crystallizing the salt from one-third its weight of water and three parts of alcohol; transparent plates are thus obtained which melt between 167° and 170°; these lose a small amount of water on long drying over sulphuric acid *in vacuo* and the melting point is thereby raised to 186°–188°. On crystallizing the anhydrous salt from absolute alcohol heavy opaque nodules are obtained, generally of the same melting point, but in one case I obtained a melting point as high as 200°. The substance, when crystallized from aqueous alcohol and then dried over sulphuric acid *in vacuo* to constant weight, melted somewhere about 186°–188° and then gave a specific rotation $[\alpha]_D^{20} = -25°.7$. (*a*) 1.0096 grams of the anhydrous salt, obtained from *d*-fructose, in 24.2283 grams water, therefore, $p = 4.00$, $d = 1.012$, gave α in 1 dcm. tube $= -1°.05$, *i. e.*, $[\alpha]_D^{20} = -25°.94$. (*b*) 1.0324 grams anhydrous salt, obtained from *d*-glucose, dissolved in 23.7041 grams of water, therefore $p = 4.17$, $d = 1.012$, gave α in a 2 dcm. tube $= -2°.16$, *i. e.*, $[\alpha]_D^{20} = -25°.7$. (*c*) 1.0122 grams anhydrous salt from *d*-glucose, dissolved in 22.6021 grams water, therefore $p = 4.28$, $d = 1.012$, gave α in 2 dcm. tube $= -2°.15$, *i. e.*, $[\alpha]_D^{20} = -25°.7$.

The free lactone was always obtained as a thick viscous gum, the specific rotation of which in 4 per cent. aqueous solution was found to be $+72°.5$; it was made from either the pure brucine or calcium salt by the usual methods. In the case of the brucine salt a hot aqueous solution was digested with an excess of either barium hydroxide or sodium hydroxide, and the precipitated brucine was thereupon separated from the cold solution by filtration, and the small amount yet remaining in solution was removed by extraction with chloroform. The lactone gum, first freed from traces of barium salt or sodium chloride by extraction with acetic ether, etc., was then dissolved in a small amount of water and heated finally under 15–30 mm. pressure in a distilling flask

in a bath kept at 100° for one-half hour. Thus 0.98 gram gum, obtained from the calcium salt, dissolved in 25 cc. water, therefore $p = 3.77$, $d = 1.011$, gave α in a 2 dcm. tube = +5°.53, whence $[\alpha]_D^{20} = +72°.5$.

The phenylhydrazide, $C_6H_{11}O_6.NHNHC_6H_5$, separates out almost quantitatively in crystalline needles on letting a solution of the lactone in 2 parts of 80 per cent. alcohol stand with an equal weight of phenylhydrazine for 24 hours at ordinary temperature. It is practically insoluble in absolute alcohol and ether and is therefore obtained sufficiently pure by simply washing with cold alcohol until snow-white. On recrystallizing 1.67 grams of the substance thus obtained from 30 cc. hot water 1.25 grams separated out, on standing overnight, in glistening needles melting from 212°–215°. A determination of the specific rotation of three different preparations of the substance in about 2 per cent. aqueous solution gave the following results: (*a*) 0.9625 gram (from *d*-fructose) in 48.7420 grams water, therefore $p = 1.93$, $d = 1.003$, gave $\alpha = -0°.52$ in a 2 dcm., tube whence $[\alpha]_D^{20} = -13°.42$. (*b*) 0.5079 gram substance (from *d*-glucose) melting at 210°–215° and 24.2031 grams water, therefore $p = 2.05$, $d = 1.003$, gave α in 1 dcm. tube = —0°.24, whence $[\alpha]_D^{20} = -12°.1$. (*c*) 0.3290 gram salt (from *d*-glucose) melting at 214° and 14.7014 grams water, therefore $p = 2.18$, $d = 1.003$, gave α in 2 dcm. tube = —0°.61, whence $[\alpha]_D^{20} = -13°.9$.

The analyses given below were carried out by José I. Rosario, who obtained the substance as one of the oxidation products of *d*-fructose in alkaline solution by air.

0.2635 gram substance gave 22.8 cc. N_2 at 20°.9 and 744.1 mm. pressure.

0.2025 gram substance gave 0.3730 gram CO_2 and 0.1164 gram H_2O.

	Calculated for $C_{12}H_{18}O_6N_2$.	Found.
C	50.32	50.33
H	6.30	6.44
N	9.79	9.73

The calcium salt, made by prolonged digestion of an aqueous solution of the lactone with powdered calcium carbonate, is soluble in about three parts of hot water and twenty parts cold water, and separates out from hot concentrated solutions on standing in short glistening needles containing five molecules of crystal water; these may be driven off by heating to 100°, but with some decomposition.

0.3293 gram air-dry salt, from *d*-fructose, gave, on ignition, 0.0360 gram CaO.

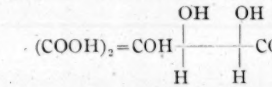
	Calculated for $C_6H_{11}O_7Ca.5H_2O$.	Found.
Ca	7.69	7.80

The specific rotation of the anhydrous salt in 4 per cent. concentration was found to be —3°.06, *i. e.*, 1.2042 grams air-dry salt, corresponding to 0.9957 gram anhydrous salt, and 23.6803 grams water, therefore $p = 4.034$, $d = 1.011$, gave α in 2 dcm. tube = —0°.25. The specific rotation of another preparation from *d*-glucose was determined as —2°.9, *i. e.*, 1.2549 gram air-dry salt and 24.3177 grams water, therefore $p = 4.09$, $d = 1.011$, gave α in a 2 dcm. tube = —0°.24.

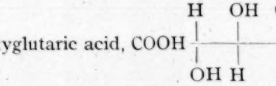
Constitution of the Acid—Conversion into d-*Trihydroxyglutaric Acid.*—It will be noticed that there is a remarkable resemblance in the properties of α-hydroxymethyl-*d*-arabonic acid and *d*-arabonic acid, as would be expected from their perfectly analogous structure. Arabonic lactone of the dextro series has a specific rotation of +73°.7 and melts at 96°; the phenylhydrazine melts at 215°, and the calcium salt crystallizes in needles with 5 molecules of crystal water;[1] the specific rotation of the calcium salt of *l*-arabonic acid has been found to be +3°.1.[2] Well-crystallized brucine, strychnine and quinine salts of *l*-arabonic acid have recently been described by Nef,[3] who also found that this acid could readily be separated from *d*-gluconic acid by means of the cinchonine salts.

[1] Ruff: Ber. d. chem. Ges., **32**, 550.
[2] Hauers and Tollens: *Ibid.*, **36**, 3306.
[3] Ann. Chem. (Liebig), **357**, 226–7.

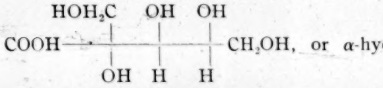
Since my α-hydroxymethyl-*d*-arabonic acid is very smoothly converted, by means of nitric acid, into a tribasic acid,



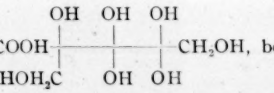
which by an asymmetric loss of carbon dioxide gives only



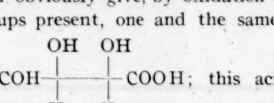
d-trihydroxyglutaric acid, COOH, it is certain that the new hexonic acid just described must be either α-hydroxymethyl-*d*-arabonic acid,



COOH, or α-hydroxymethyl-*d*-ribonic acid,



COOH, both of which compounds can obviously give, by oxidation of the two primary alcohol groups present, one and the same tribasic acid,

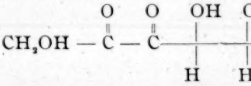


; this acid might, by loss of carbon dioxide, give both ribo- as well as *d*-trihydroxyglutaric acid, but remarkably enough it loses carbon dioxide asymmetrically and therefore gives only one of the two trihydroxyglutaric acids, namely, the optically active one. I consider the other possible formula for my new hexonic acid, namely, that of α-hydroxymethyl-*d*-ribonic acid, as extremely improbable, since *d*-ribonic lactone gives, with alkaloids or bases, practically no crystalline derivatives other than the low melting phenylhydrazide and the cadmium salt.[1]

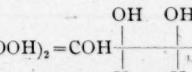
The formation of α-hydroxymethyl-*d*-arabonic acid from

[1] Fischer and Piloty: Ber. d. chem. Ges., **24**, 4216.

α- and β-*d*-glutose, as predicted by Nef,[1] obviously takes place by a transformation of the 2-3-osone,



(which is common to both these sugars) by an *entire* asymmetric benzilic acid rearrangement; the constitution of the glutose sugars as 3-ketohexoses is thereby also definitely established.

Twenty-nine grams of air-dry calcium α-hydroxymethyl-*d*-arabonate treated with the calculated amount of oxalic acid gave, in the usual way, 18.52 grams of the crude lactone gum; this was heated[2] with 62.5 cc. of nitric acid (sp. gr. 1.2) for four days between 45° and 55°. The water and excess of nitric acid were then removed by several distillations under 15–25 mm. pressure in a bath kept at 50° (adding water after each operation, etc.). A very thick gum, 17.59 grams, remained, which consisted mainly of the above-mentioned tribasic acid,  , since on dissolving in 100 cc. water, and heating for seven hours under a reflux condenser in a bath kept between 120°–130°, streams of carbon dioxide were evolved. The aqueous solution was then digested with powdered calcium oxide in half-gram portions until no more calcium oxalate was deposited; the addition of lime to the aqueous filtrate was then continued until on long boiling the solution remained permanently alkaline. Carbon dioxide was then passed through the solution to get rid of the excess of calcium hydroxide, and a very careful examination of the rather difficultly soluble calcium salts obtained on concentrating the aqueous filtrate established with certainty the presence of only *d*-trihydroxyglutaric acid besides some unchanged α-hydroxymethyl-*d*-arabonate of calcium; not a trace of the isomeric ribotrihydroxyglutaric

[1] Ann. Chem. (Liebig). **357**, 298.

[2] Kiliani: Ber. d. chem. Ges. **38**, 2671, 3624; **40**, 1238.

acid, which is optically inactive by intramolecular compensation, and the properties of which are well known,[1] could be found. The calcium salt of *d*-trihydroxyglutaric acid[2] separates out from the hot concentrated aqueous solutions as a gum; it is therefore best obtained in the crystalline form from moderately dilute solutions on scratching and standing; 6.98 grams of the salt were thus obtained in microscopic crystals, which, on recrystallization, gave 5.37 grams. A portion of this salt, 3.020 grams, dried four days over sulphuric acid *in vacuo*, lost 0.440 gram H_2O; and 0.3718 gram of the anhydrous salt gave, on ignition, 0.0933 gram CaO.

	Calculated for $C_5H_6O_7Ca.2H_2O$.	Found.
H_2O	14.26	14.56
	Calculated for $C_5H_6O_7Ca$.	**Found.**
Ca	18.34	17.92

The remainder of the salt was now converted, by means of oxalic acid, into the free acid; the crude product, 3.73 grams hard gum, on being dissolved in a small amount of acetone and adding dry ether, gave at first a gummy precipitate which was soon transformed by scratching into 2.05 grams of the white crystalline acid, $C_5H_8O_7$,[3] melting sharply at 175°. The specific rotation was found to be +28°.3; *i. e.*, 0.4075 gram and 8.1553 grams water (therefore $p = 4.75$, $d = 1.023$) gave $\alpha = +1°.38$ in a 1 dcm. tube.

That the gum left in the acetone-ether filtrate contained no ribotrihydroxyglutaric acid is certain from the following: It was first dissolved in water and freed from solvents, etc., by distillation under 25 mm. in a weighed flask which was heated finally on a boiling water bath. The gum, 1.48 grams, dissolved in 29.72 grams water ($p = 4.74$ and $d =$

[1] Fischer and Piloty: Ber. d. chem. Ges., **24**, 4222.

[2] Boutroux: Compt. Rend., **127**, 1224. Lippmann: Ber. d. chem. Ges., **26**, 3060.

[3] Lippmann (*Loc. cit.*) first obtained this acid and gave the melting point 125° and $[\alpha]_D^{20} = +20°.8$. Ruff (Ber. d. chem. Ges., **32**, 550) then obtained the same substance from *d*-arabinose and gave the melting point 128° and $[\alpha]_D^{20} = +22°.8$. Recently Tollens and Rorive (Z. Ver. d. Zuckerind., **1909**, 579) have described the acid more fully; after repeated recrystallization they obtained a substance melting from 150°–160° (though not sharply) and giving $[\alpha]_D^{20} = +27°.6$.

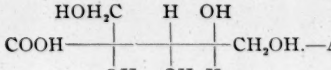
1.013) gave $\alpha = +1°.45$ in a 1 dcm. tube, whence $[\alpha]_D^{20} = +30°.2$.

The crystalline acid obtained was further identified as *d*-trihydroxyglutaric acid by its conversion, by means of potassium carbonate, into the characteristic potassium salt.[1] The anhydrous salt was obtained in long transparent needles, giving a specific rotation of $-9°.5$; *i. e.*, 0.7895 gram and 19.5524 grams water (therefore $p = 3.88$ and $d = 1.017$) gave $\alpha = -0°.75$ in a 2 dcm. tube.

The aqueous filtrate from the 6.98 grams calcium *d*-trihydroxyglutarate mentioned above gave a further crop, 1.91 grams, of the same salt; from this 1.4 grams of the crude acid giving with acetone and ether only 0.5 gram of the crystallized acid, melting at 170°, were obtained. The latter showed a specific rotation of $+24°.15$, *i. e.*, 0.2229 gram and 6.6592 grams water (therefore $p = 3.23$, $d = 1.023$) gave $\alpha = +0°.80$ in a 1 dcm. tube. The noncrystalline gum still left in the solvent used gave a specific rotation of $+32°.5$; *i. e.*, 0.7 gram gum and 16.51 grams water (therefore $p = 4.06$ and $d = 1.023$) gave α in a 1 dcm. tube $= +1°.35$.

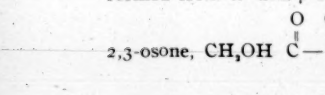
Finally the remaining noncrystalline lime salts left in the aqueous filtrate from the two crops of lime salts just mentioned yielded, on removing the calcium with oxalic acid, etc., a total of 1.97 grams acid gum, which gave a specific rotation of $+38°.8$; *i. e.*, 1.97 grams gum and 49.47 grams water (therefore $p = 3.82$) gave $\alpha = +1°.5$ in a 1 dcm. tube. It is therefore obvious that all the material obtained from the oxidation of α-hydroxymethyl-*d*-arabonic lactone after splitting off carbon dioxide, etc., was strongly dextrorotatory.

d-*Galactose—α-Hydroxymethyl*-d-*lyxonic Acid*,



—As already mentioned, 80.2 per cent. of *d*-galactose is converted by alkaline hydrogen peroxide into formic acid; a small amount, 4.65 per cent., of car-

[1] Tollens and Rorive: *Loc. cit.* See also Will and Peters: Ber. d. chem. Ges., **22** 1698.

bon dioxide is also formed. The remaining fifteen per cent. of the sugar is converted into tar and into glycollic acid and a new hexonic acid which, by analogy and from its properties, is considered to be α-hydroxymethyl-*d*-lyxonic acid; it is formed from α- and β-*d*-galtose by oxidation to the common 2,3-osone,  which then, by an entire asymmetric benzilic acid rearrangement, gives only one of the two isomeric acids theoretically possible.[1]

The nonvolatile gums obtained, after standing six days, etc., from the oxidation of 100 grams (in four portions) of *d*-galactose, melting at 167°–168°, with six molecules of hydrogen peroxide and nine molecules of sodium hydroxide weighed only 7.13 grams, as a decided amount of tar was formed. Threefold extraction of this gum with 300 cc. ether gave 4.43 grams of soluble and fairly mobile acid gum, which, by titration with 0.1 N alkali, was shown to consist of about 85 per cent. glycollic acid and 15 per cent. hexonic acid lactone. Glycollic acid was removed in great part from the mixture by means of the difficultly soluble strychnine salt, 10.88 grams of the pure salt, corresponding to 2.05 grams free acid, being actually obtained. The new hexonic acid was characterized by its brucine salt, crystalline plates melting from 171°–175° (1.9 grams obtained from alcohol), and especially by the quinine salt which crystallizes from hot water in long needles, is very difficultly soluble in this solvent in the cold, and melts at 213° (3.4 grams obtained). Finally the crude acid gum, obtained from either of these salts, gave very rapidly, on standing in the cold with 2 parts of 80 per cent. alcohol and 1 part of phenylhydrazine, a crystalline phenylhydrazide which became snow-white on washing with cold alcohol, melted sharply at 144°, and gave the following results on analysis:

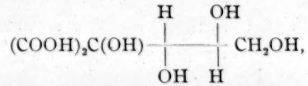
0.1577 gram gave 13.4 cc. nitrogen at 21° and 745.7 mm. pressure.

[1] Nef: Ann. Chem (Liebig), **357**, 298.

0.1122 gram gave 0.0789 gram H_2O and 0.2081 gram CO_2.

	Calculated for $C_{12}H_{18}O_8N_2$.	Found.
C	50.32	50.49
H	6.30	7.87
N	9.79	9.50

From a comparison of the properties of the derivatives of my new hexonic acid with those of *d*-lyxonic and *l*-xylonic acids, as well as by analogy from my experiments with the members of the *d*-glucose series, I have come to the conclusion that α-hydroxymethyl-*d*-lyxonic acid must be present. Accordingly the new acid must be converted by oxidation with nitric acid into a tribasic acid,



which, by loss of carbon dioxide, must give either *d*-trihydroxyglutaric or xylotrihydroxyglutaric acid. It is therefore my intention to carry out this oxidation experiment on a large scale in the near future. Moreover, instead of using *d*-galactose for the preparation of α-hydroxymethyl-*d*-lyxonic acid, I intend to start with α- and β-*d*-galtose, from which I expect to obtain this acid in splendid yield.

Glycol, Glycollic Acid and Formic Acid in the Presence of Alkaline Hydrogen Peroxide.

The following experiments show that ethyleneglycol, as well as glycollic acid, are very slowly oxidized by alkaline hydrogen peroxide, and give small amounts of formic and carbonic acids but no trace of oxalic acid. Formic acid, on the other hand, is not perceptibly oxidized. Since no trace of any other hydroxy acid, such as glycerinic, trihydroxybutyric acid, *d*-mannonic or *d*-gluconic acid was ever observed in my oxidation experiments with *d*-glucose and *d*-fructose, I have not as yet proved that these acids are also only slightly effected by alkaline hydrogen peroxide, but it is my intention to carry out such experiments soon.

(a) Two grams of ethyleneglycol, boiling at 193°, dissolved in 120 cc. of three per cent. hydrogen peroxide (three molecules), were added to a normal solution containing 7.24 grams (four molecules) of potassium hydroxide. The mixture stood for four days at room temperature; on working up as usual 0.13 gram formic acid, 1.25 grams unchanged glycol, and no trace of oxalic acid were obtained.

(b) Glycollic acid, two grams, was dissolved in 73 cc. three per cent. hydrogen peroxide (2.5 molecules) and added to a normal solution containing 4.48 grams (3 molecules) of potassium hydroxide. On working up after standing four days, 0.133 gram carbon dioxide and 0.125 gram of formic acid, besides 1.36 grams unchanged acid, were found. This shows that glyoxylic acid, which must first be formed by oxidation, gives equal molecular proportions of formic and carbonic acids, but no oxalic acid on further oxidation.[1]

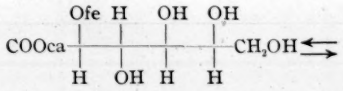
(c) On allowing a mixture of 67 cc. three per cent. hydrogen peroxide (1.5 molecules), 1.71 grams formic acid, and 4.48 grams potassium hydroxide (2 molecules) in normal solution to stand for 3 days at ordinary temperature only a minute amount, not over 0.01 gram, of carbon dioxide was formed.

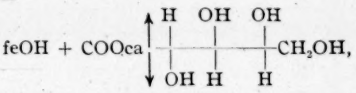
Part II. On the Behavior of Hydrogen Peroxide towards Hexoses in the Presence of Traces of Iron Salts.

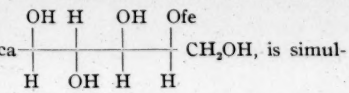
In 1894 Fenton[2] observed that tartaric acid dissolved in three per cent. hydrogen peroxide is rapidly oxidized if a trace of ferrous sulphate be added; similar observations were also made by him in the case of many hydroxy acids as well as polyatomic alcohols. Cross, Bevan and Smith,[3] as well as Morrell and Crofts,[4] have applied Fenton's reaction to the carbohydrates and have determined the character of some of the oxidation products found. By the use of hydrogen peroxide and small amounts of ferric acetate Ruff[5] was also able to convert the hexonic and pentonic acids, with loss of carbon dioxide, into pentose and tetrose sugars.

[1] Cf. Denis: THIS JOURNAL, **38**, 361.
[2] J. Chem. Soc., **65**, 899; **75**, 1; **77**, 69, 1294.
[3] *Ibid.*, **73**, 463.
[4] *Ibid.*, **75**, 786; **77**, 1219; **81**, 666; **83**, 1284; **87**, 280.
[5] Ber. d. chem. Ges., **31**, 1573; **33**, 550, 3672; **33**, 1798; **34**, 1362.

Fenton supposed that the ferrous salt had a specific effect in the reactions under consideration, whereas Ruff attributes the catalytic effect to the presence of the ferric salt; my own observations show that the reactions go equally well in the presence of traces of a ferric or ferrous salt. It was found that whether a ferrous or ferric salt be used, the iron in solution in hydrogen peroxide is always in the ferrous condition as long as there is simultaneously present a reduceable substance (*e. g.*, sugar, etc.); as soon as the latter is consumed the iron is oxidized to the ferric condition. It is evident from Nef's work[1] on alcohols and their salts that the addition of the iron salt serves simply to give, through intermediate salt formation, an increase in the percentage of existing methylene dissociation. The conversion by Ruff of calcium *d*-gluconate into *d*-arabinose, etc., therefore simply proves that the iron salt,

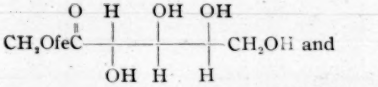




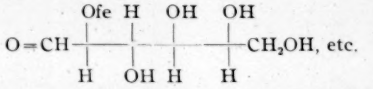
is mainly formed, which then, in the dissociated condition, oxidizes to the α-keto acid with subsequent spontaneous loss of carbon dioxide, and formation of *d*-arabinose, etc. Obviously only a trace of iron salt is necessary, just as in the conversion of alcohol into ether by sulphuric acid. Since, moreover, Ruff[2] also proved that a small amount of 4-ketogluconic acid is formed in the reaction we must conclude that another iron salt,  , is simultaneously present; from a theoretical standpoint there

[1] Ann. Chem. (Liebig), **318**, 138; **335**, 312; **357**, 294–312.
[2] Ber. d. chem. Ges., **32**, 2269.

is the possibility of formation of five different iron salts with calcium *d*-gluconate.[1] The fact observed by Morrell that *d*-fructose and *d*-glucose give with one molecule of hydrogen peroxide and traces of iron salts a fair amount of 1,2-glucosone therefore simply proves that the iron salts formed by these sugars possess the constitution



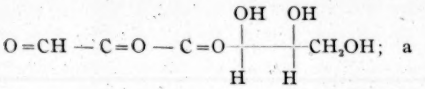
and



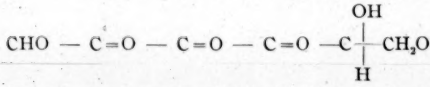
I therefore began a further study of the action of hydrogen peroxide towards various sugars in the presence of small amounts of ferrous or ferric sulphate from this standpoint. Morrell and Crofts used from one to four molecules of hydrogen peroxide in their experiments with *d*-glucose, *d*-fructose and *d*-galactose, and isolated, besides the 1,2-hexosone, glycollic, glyoxylic and oxalic acids as definite oxidation products. They state also that erythronic acid (trihydroxybutyric acid) is formed from *d*-glucose and *d*-fructose, especially when 4 molecules of hydrogen peroxide were used. The various isomeric trihydroxybutyric acids are now known to give very striking and easily identified derivatives.[2] I tried, by repeating Morrell's experiment, to determine which of these acids were actually present, but never found any of them. I am therefore of the opinion that a keto acid or a mixture of keto acids containing four carbon atoms was actually present instead of erythronic acid, but I was unable to prove this by the isolation of crystalline derivatives. It is obvious that 1,2-glucosone, the common oxidation product of dextrose and laevulose, might easily give by further salt formation, subsequent oxidation, etc., a 1,2,3-osone,

[1] Cf. Nef: Ann. Chem. (Liebig), **357**, 255, 283.

[2] Ruff: Ber. d. chem. Ges., **32**, 3674; **34**, 1362. Nef: Ann. Chem. (Liebig), **357**, 247. Anderson: THIS JOURNAL, **42**, 423.



$O=CH-C=O-C=O$ (OH, OH / H, H) $-CH_2OH$; a 1,2,3,4-osone,



$CHO-C=O-C=O-C=O-C$ (OH / H) $-CH_2OH$; etc., and

the decisive results which I have obtained with *d*-galactose, *d*-glucose and *d*-fructose by using an excess (14 molecules) of hydrogen peroxide in the presence of ferrous or ferric sulphate can only be explained on the assumption that intermediate products of this character are first formed. The three sugars named burn under these conditions completely to give varying amounts of formic, carbonic and oxalic acids; my experiments prove also that the formic acid first formed is readily further oxidized to carbon dioxide by hydrogen peroxide and iron salts, whereas oxalic acid remains practically unaltered in the presence of these reagents, Now glycol, glycerol and their oxidation products, diose and triose, never give more than minimal traces of, if any, oxalic acid when treated with hydrogen peroxide and iron salts; they burn exclusively to formic and carbonic acids. I consider therefore that the formation of large amounts of oxalic acid, from 18 to 27 per cent., from the hexoses named, must be due to a direct hydrolysis of such polyhexosones first formed from the hexoses by oxidation.

On the Quantitative Oxidation of Hexoses with an Excess of Hydrogen Peroxide (14 Molecules) in the Presence of Iron Salts.

The sugar to be oxidized was dissolved in water, mixed with an aqueous solution containing 0.25 to 0.75 of a molecule of ferrous or ferric sulphate, and an excess (14 molecules) of three per cent. hydrogen peroxide was then slowly added through a separatory funnel. The oxidation took place with some evolution of heat at first, but the mixture was allowed to stand for 20 hours at ordinary temperature in the regular apparatus used for the determination of carbon dioxide men-

tioned under Part I. All the carbon dioxide formed in the oxidation was collected as usual in the barium hydroxide cylinders. After removing the sulphate present by addition of the calculated amount of barium hydroxide, etc., the free formic acid present in the aqueous solution was removed by distillation at reduced pressure as described under Part I. The iron present in the water solution of the nonvolatile residue was then precipitated by ammonium sulphide and the filtrate, freed from hydrogen sulphide by boiling, then gave with ammonia and calcium chloride a precipitate of calcium oxalate, which was purified by dissolving in dilute hydrochloric acid, reprecipitating with ammonia, adding acetic acid, filtering and weighing, after drying at 100°, as the salt $C_2O_4Ca.0.5H_2O$.

On adding slowly 190 cc. of a 2.84 per cent. solution of hydrogen peroxide to an aqueous solution of 2 grams *d*-galactose and 2.04 grams ferric sulphate, $Fe_2(SO_4)_3.5H_2O$, in 40 cc. water, a noticeable evolution of heat took place within the first hour, which was controlled by keeping the mixture in a bath at 20°. Entirely similar experiments were carried out with 2 grams *d*-fructose and 2 grams *d*-glucose with the following results after standing 20 hours at room temperature:

	Carbon dioxide.		Formic acid.		Oxalic acid.	
	Grams.	Per cent.	Grams.	Per cent.	Grams.	Per cent.
d-Galactose,	2.03	69.28	0.092	3.0	1.13	26.9
d-Glucose,	2.08	70.98	0.092	3.0	0.70	16.66
d-Fructose	2.13	72.69	0.024	0.77	0.76	18.89

A quantitative experiment with 2.87 grams *formic acid* and 3.7 grams ferric sulphate (0.25 molecule) in 80 cc. water showed that the oxidation took place at once on adding 69 cc. of a 2.87 per cent. solution of hydrogen peroxide; after standing seven hours 2.14 grams of carbon dioxide, 78.1 per cent., had been formed and only 0.32 gram of free formic acid was recovered; the solution contained ferric formate.

A similar experiment with 2 grams crystallized *oxalic acid* and 0.97 gram ferric sulphate (0.25 molecule) in 70 cc. water, gave, after adding 24 cc. of a 2.3 per cent. solution of hydrogen

peroxide and standing six hours only, 0.04 gram carbon dioxide, *i. e.*, 3.1 per cent., besides 1.91 grams unchanged oxalic acid.

When *glycollic acid*, 2 grams, and ferric sulphate, 1.63 grams (0.25 molecule), were dissolved in 45 cc. water and treated with 90 cc. of a 2.95 per cent. solution of hydrogen peroxide (3 molecules), the amount of carbon dioxide found, after standing 20 hours, was 1.96 grams, or 84.84 per cent.; in addition 0.396 gram formic acid, 10.75 per cent., but no trace of oxalic acid, could be found.

Two grams of *ethyleneglycol*, which has been proved by Fenton[1] to give glycollic aldehyde (diose) as an intermediate product, gave, when treated in aqueous solution with 1.75 grams ferric sulphate and 228 cc. of a 2.9 per cent. solution of hydrogen peroxide (6 molecules), after standing 96 hours, 2.54 grams carbon dioxide, 89.78 per cent., besides 0.24 gram formic acid, but no trace of oxalic acid.

Finally two grams of glycerol (which had been shown by Fenton to give first glycerinic aldehyde), 1.3 grams ferric sulphate (0.25 molecule), and 210 cc. of a 2.44 per cent. solution of hydrogen peroxide (7 molecules) gave, after standing 24 hours, 1.99 grams carbon dioxide (67.79 per cent.), 0.74 gram formic acid, 24.77 per cent., and just a trace, less than 0.001 gram, of oxalic acid.

Finally, I give here a brief summary of some quantitative experiments carried out with *d*-galactose and *d*-fructose with from 1 to 4 molecules of hydrogen peroxide in the presence of small amounts of iron salts. It will be seen that even under these conditions much formic and carbonic acids are formed, a fact which has been overlooked by Morrell in his work; oxalic acid, on the other hand, was present only in small amounts.

d-*Galactose and Four Atoms Oxygen.*—Twenty-five grams *d*-galactose, 60 cc. water, 0.2 gram iron vitriol, $FeSO_4.7H_2O$, and 646 cc. of a 2.9 per cent. solution of hydrogen peroxide gave, after standing 14 hours, 5.05 grams carbon dioxide and 6.5 grams formic acid. Treatment of the nonvolatile gum,

[1] J. Chem. Soc., 75, 1.

17 grams, with an excess of powdered calcium carbonate, etc., gave only 0.85 gram calcium oxalate, corresponding to 0.59 gram crystallized oxalic acid, and addition of alcohol to the concentrated aqueous filtrate (after decolorizing with charcoal, etc.), gave 15.05 grams precipitated calcium salts containing 12.07 per cent. calcium and reducing Fehling's solution; only 1.51 grams dark neutral gum was found in the aqueous alcoholic filtrate. On precipitating the calcium in the soluble salts with the calculated amount of oxalic acid, etc., I was able to prove the presence of a small amount of glycollic acid by the isolation of the characteristic strychnine salt (6.0 grams, corresponding to 1.1 grams acid), but obtained no other definite products by means of brucine or phenylhydrazine.

In another experiment in which 10 grams of *d*-galactose, 0.1 gram of iron vitriol, 20 cc. of water and 202 cc. of 1 per cent. hydrogen peroxide (1 molecule) were used, the amount of formic acid obtained, after standing 24 hours, was 0.33 gram; a large amount of neutral nonvolatile gum was also obtained, but this could not be handled. A similar experiment with 2 molecules of the oxidizing agent gave 0.44 gram carbon dioxide and 0.644 gram of formic acid from 10 grams of *d*-galactose.

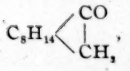
d-*Fructose and Four Atoms Oxygen.*—A mixture of 25 grams of laevulose, 0.65 gram iron vitriol, 100 cc. of water and 648 cc. of a 2.89 per cent. solution of hydrogen peroxide gave, after standing five days, precipitating the sulphuric acid by means of barium hydroxide, etc., 22 grams of dark brown gum; this was converted by heating for 8 hours with 66 cc. of acetic anhydride, etc., into 28.1 grams of acylated gum (after heating to 100° under 20 mm. pressure) of which, on threefold thorough digestion with 500 cc. of ether each time, only 7.08 grams dissolved, leaving 21.8 grams of granular, insoluble, dark brown tar. The ether-soluble acylated gums were proved to contain glycollic acid on hydrolysis with water.

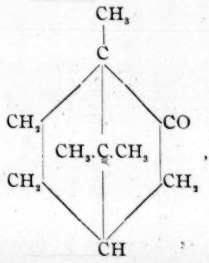
To Dr. Nef, for his guidance and interest in the above work, I am very grateful.

CAMPHOR.[1]

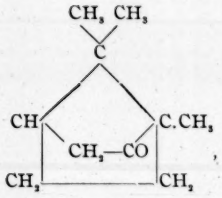
By G. Blanc.

The formula now assigned to camphor and which may be written, as is most convenient, in either of the three forms,





or



appear to follow quite naturally from the known properties of camphor and it does not seem as if its derivation should have caused any particular difficulty. But such a supposition is quite erroneous for, as a matter of fact, before the truth was definitely established an enormous amount of work had to be done and several constitutional formulas which, as the problem was developed, appeared successively to be more probably the correct ones had to be considered. This considerable difficulty in the working out of a problem which, now that it is solved, seems quite simple, was due to several

[1] Address delivered before the Chemical Society of France on March 20, 1909; and published in the Bull. Soc. Chim., May 5, 1909.

causes, the two principal ones of which were, beyond doubt, the then very incomplete knowledge possessed by chemists, and which is still very limited, as to the behavior of heterocyclic chains, and especially the ease with which the camphor molecule and its direct decomposition products undergo transformations.

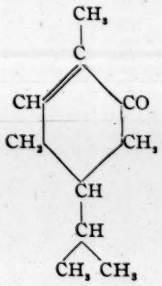
To these unfortunate transformations, which were then unsuspected, were due the bitter polemics that for several years divided chemists, perfectly well-established experimental facts leading to radically false theoretical deductions.

In this address I will attempt to demonstrate the subtlety of the later researches which finally led to the establishment of the truth, and to bring out the part taken by each investigator in this work. I wish at the outset to beg indulgence for having to enter into personalities and to mention some of my colleagues only to say that they were in error.

Moreover, the same thing has happened to me and, indeed, it can be said that no one who took an active part in the controversy escaped a similar misadventure.

I will begin with a very brief résumé of the whole question, and in order not to go too far back I will take up the first formula which really deserves any attention.

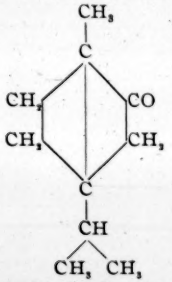
Kekulé's formula,[1]



took into account, at the time when it was proposed, certain very important facts which could serve as the basis for es-

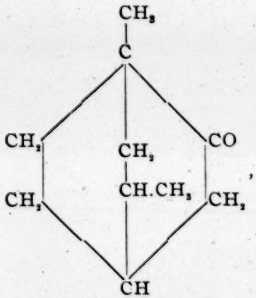
[1] See Wurtz's dictionary, second suppl., p. 931.

tablishing a constitutional formula, *viz.*, the transformation of camphor into *p*-cymene by the action of phosphoric anhydride, and into carvacrol by means of iodine. But it was not long before it was seen that the camphor molecule probably contains no double bond, for no stable addition product is known. On the basis of this observation, several formulas were proposed in which it was attempted to account for the two missing hydrogen atoms by the presence of a bond between two nonadjacent carbon atoms, *e. g.*,



Bredt's first formula.

Certain stereochemical considerations led Bouveault to propose a formula in which the extra bond was placed somewhat differently, *viz.*, the carbon atom to which was attached the methyl group was united, not to the opposite para carbon atom, but to a carbon of the isopropyl group:



Bouveault's first formula.

As we shall see later, this idea was not a fortunate one, for a second solution presented itself, *viz.*, union with the tertiary carbon of the isopropyl group; it is extremely regrettable that Bouveault, ill inspired, did not think of it, for this proved to be the correct solution. But, to be sure, he could not guess this.

Nevertheless, the problem was by no means definitely solved, and the new facts observed in different directions, especially in connection with camphoric acid, did not seem to advance its solution (in fact, just the contrary) or to crystallize opinions as to the relative merits of the Kekulé formula and its modifications.

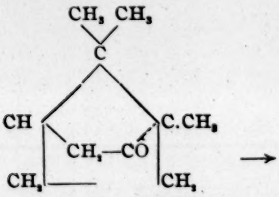
It seemed, in fact, that camphoric acid, thanks to its singular properties, offered a new and interesting field for investigation and that the solution of the problem was to be sought through this compound.

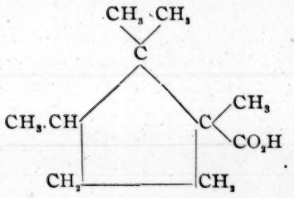
Camphor results from the union of two pentagonal rings to form a third hexagonal one and we know that the derivation of a formula for such a substance cannot be effected easily. Logically, the problem must be simplified by studying a product derived directly from camphor and containing but one ring.

We shall see that camphoric acid alone could furnish the desired result.

In fact, we have three principal methods available for effecting the desired change in the camphor molecule, *i. e.*, the breaking open of one chain, leaving a monocyclic compound.

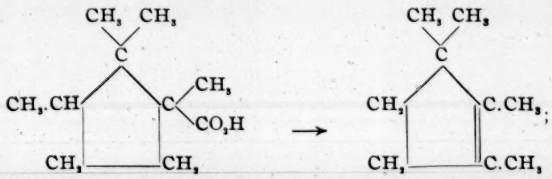
(1) The addition of the elements of water by means of alkalis, under proper conditions, with the formation of campholic acid:





Now that we know the correct formula for campholic acid, it is not difficult to see why the investigations undertaken to determine its constitution, especially that of Guerbet,[1] were doomed to failure. This acid contains a carboxyl group attached to a tertiary carbon atom and the analytical methods usually employed (bromination, then removal of hydrobromic acid and oxidation) cannot be used.

The study of the unsaturated hydrocarbon campholene, derived from this acid by the loss of $CO + H_2O$, might lead to interesting conclusions, but campholene is itself already a transformation product:



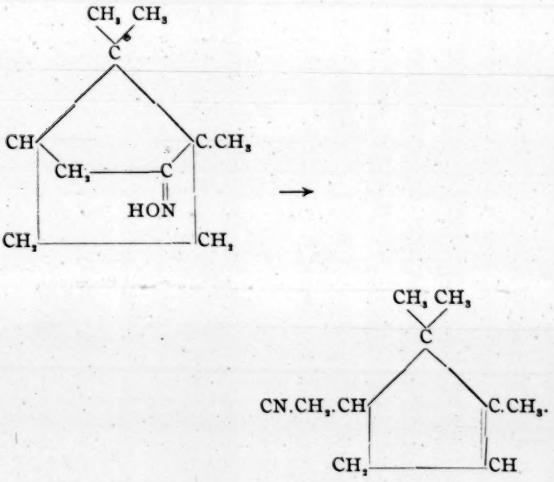
and, moreover, the methods employed by Guerbet (heating with fuming hydriodic acid) bring about other and still more deep-seated changes.

Misled by these numerous and unsuspected transformations, Guerbet could not, therefore, draw correct conclusions.

(2) The opening of one ring (the same as in the case of the campholic acid, although in a slightly different manner),

[1] Thesis, Paris, 1894.

starting from camphoroxime. The normal reaction is represented as follows:

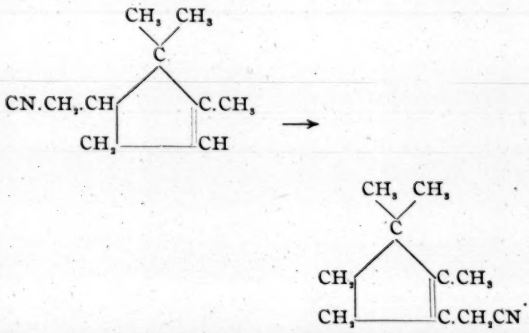


The product so obtained (α-campholenonitrile) can, without difficulty, be converted into the acid, which lends itself more easily to investigation than campholic acid.

Unfortunately, such investigation is extraordinarily difficult, and the chemists (Béhal,[1] Tiemann[2]) who have devoted themselves to it have been able to obtain only incomplete results which, though very interesting, to be sure, are not decisive. For, as a matter of fact, the conversion of camphoroxime into α-campholenonitrile is always accompanied by the formation in greater or less quantity, by a process which I shall explain later in connection with the α- and β-cam-

[1] Compt. Rend., **120**; Bull. Soc. Chim., [3] **13**, 844.
[2] Dict. Chim. Gén., **28**, 2166; **29**, 3806; **30**, 242, 321, 404.

pholytic acids, of a transformation product, β-campholenonitrile:



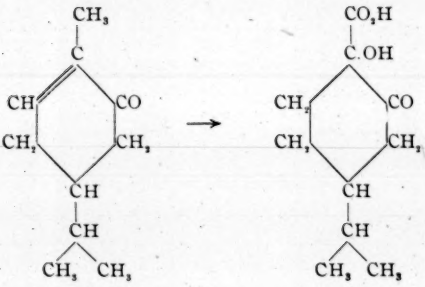
Then, too, the study of the two resulting acids (α- and β-campholenic acids) bristles with difficulties, owing to numerous molecular transformations.

(3) There remains, then, camphoric acid, whose relation to camphor is well known. It is derived from the latter by oxidation with nitric acid:

We must not assume that the formula is the evidence itself, or that it was at once accepted by every one.

Indeed, camphoric acid would seem, from this formula, to be a dicarboxylic acid. Now, the properties of the two acid groups are so different that Friedel[1] assumed that the extreme feebleness of one of them was due to its being, not a carboxyl group, but an acid hydrogen between two electronegative groups. Kekulé's formula lends itself well to such an assumption:

1 Wurtz's Dict., second suppl., p. 931; and Compt. Rend., **113**, 825.



At first sight, such a formula seemed very alluring, but the facts which daily accumulated soon overthrew it.

First, it was shown directly that camphoric acid really does contain two carboxyl groups.

This was demonstrated simultaneously in several ways; I will cite only one very decisive proof.

Camphoric acid is extremely asymmetric, the two acid groups having entirely different properties; thus, a monamide corresponding to each of them (α- and β-camphoramic acids) is known.

Each of these α- and β-camphoramic acids, when treated with bromine and sodium hydroxide (Hofmann's reaction), is converted into an amino acid by the loss of carbon monoxide.[1] Each of the amide groups consists, therefore, of the $CO.NH_2$ grouping.

We admit, then, that the relation between camphor and camphoric acid,

is sufficiently proved.

This reaction yields, of course, but one acid, since both the

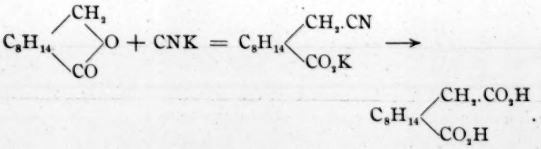
[1] Noyes: This Journal, **16**, 317, 500; **17**, 421; Dict. Chim. Gén., **28**, 547; This Journal, **18**, 686; Dict. Chim. Gén., **29**, 2326.

CH_2 and CO groups of the complex $—CH_2.CO—$ are converted into carboxyl groups.

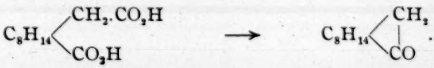
But, furthermore, to the clean-cut conversion of camphor into camphoric acid corresponds the no less well-defined conversion of this acid into camphor.

Haller[1] has shown that camphoric anhydride is converted, by reduction with sodium amalgam, into a lactone, campholide:

This campholide, when treated with potassium cyanide, goes over into the nitrile of an acid which Haller called homocamphoric acid:



Finally, this homocamphoric acid can be converted into the lead salt which, when heated, yields camphor:

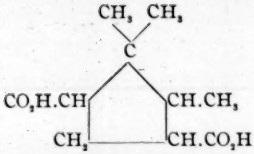


The whole question now resolved itself into the determination of the constitution of camphoric acid. This problem has been the subject of considerable investigation, and it was only after several years of earnest work that it was solved.

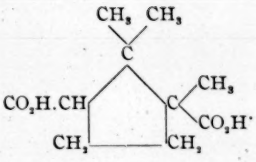
In order to discuss it at its most interesting stage, we shall take up the question as it stood towards the end of the year 1897.

At that time two formulas were under consideration, Tiemann's and Bredt's second formula:

[1] Compt. Rend., **122**, 293, 446.



Tiemann's formula.

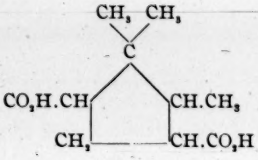


Bredt's formula.

Let us see how these formulas were derived.

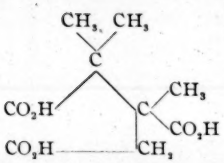
Tiemann's formula[1] is derived from that which he assigned to camphor from its relation to pinene. This point being quite complex and beyond the scope of the subject which I propose to consider, I shall not discuss it. I shall merely state that it was very soon found that this formula was not in harmony with certain very interesting facts, especially the formation, from camphoric acid, by oxidation, of camphoronic acid whose synthesis had just been effected by Perkin, Jr., and J. F. Thorpe.[2]

In act, the compound



cannot give

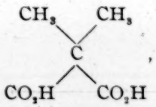
[1] Dict. Chim. Gén., **28**, 1079.
[2] J. Chem. Soc., **91**, 1169.



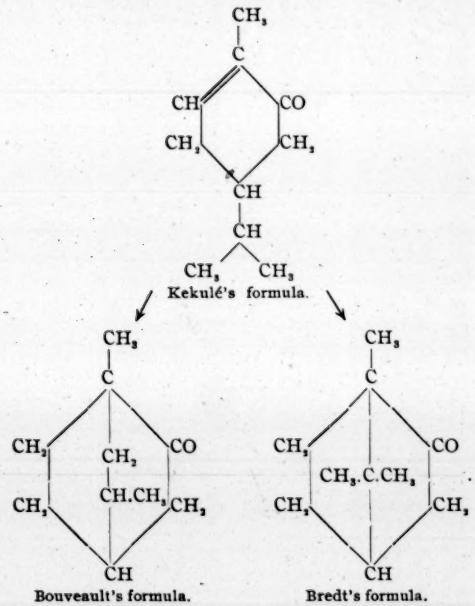
There remains, then, Bredt's formula.

As you will remember, we saw how Bouveault modified Kekulé's camphor formula by changing the double bond, the existence of which was very doubtful, into a cross bond, properly placed.

A short time after the publication of Bouveault's paper, Koenigs announced that when camphoric acid is oxidized with potassium permanganate, dimethylmalonic acid,



is obtained. Camphoric acid and, consequently, camphor must then contain the grouping ; this extremely important observation led Bredt to modify Bouveault's formula by making the union through the tertiary carbon atom of the isopropyl group:



Such is the origin of Bredt's formula; a change of the Kekulé formula by a modification of Bouveault's process, as the result of an observation by Koenigs.

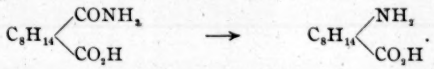
We shall see by what follows that, personally, Bredt brought forward not a shadow of confirmation of his formula.

The resulting formula for camphoric acid accounted quite well at the time for all the known properties of the acid (oxidation products, interpretation of the different energies of the two carboxyl groups, etc.).

At that moment an event took place which had extremely remarkable consequences. W. A. Noyes[1] showed that β-cam-

[1] *Loc. cit.*

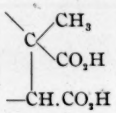
phoramic acid is converted by bromine and sodium hydroxide into an amino acid, dihydroaminocampholytic acid:



The latter is converted by nitrous acid into an unsaturated acid, campholytic acid, $C_8H_{13}CO_2H$.

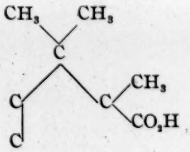
This is an α,β-unsaturated acid, for it is reduced by sodium and alcohol to a saturated acid, $C_8H_{15}CO_2H$. The latter, when treated with bromine, takes up the halogen in the α-position and the resulting bromo acid gives again, with potassium hydroxide, campholytic acid. All these facts can be explained only if we assume the presence of the grouping

in campholytic acid, and, as a consequence, of the group



in camphoric acid.

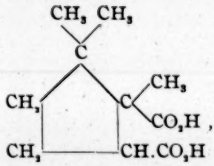
These remarkable experiments, in conjunction with the work of L. Balbiano,[1] who demonstrated the presence of the complex



in camphoric acid, led Bouveault to propose a new formula for camphoric acid.

[1] Dict. Chim. Gén., **28**, 1507; Gazz. Chim. Ital., **26**, 1; and Dict. Chim. Gén., **30**, 289, 1901.

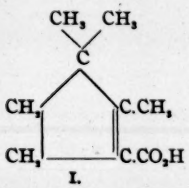
This formula,



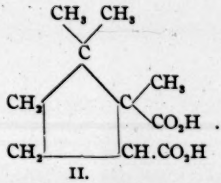
thus obtained, seemed to explain all the more important analytical facts and, consequently, to represent the true constitution of camphoric acid.

My own investigations, which I had undertaken a year before, independently of Bouveault, led me to an identical conclusion.[1]

Camphoric anhydride, treated in chloroform solution with aluminium chloride, yields, by the loss of carbon dioxide, the same campholytic acid which Noyes obtained from β-camphoramic acid; I was able to show definitely and with absolute certainty that this acid had the constitution (I):



I.



II.

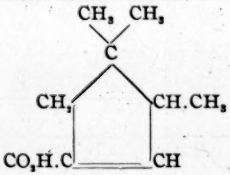
Hence camphoric acid must necessarily be represented by the formula (II).

This point was therefore perfectly cleared up, and the new formula had already secured many adherents when a new article by W. H. Perkin, Jr., on this very point again placed the whole matter in question.[2]

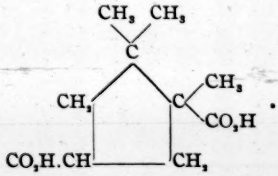
According to W. H. Perkin, Jr., Noyes's campholytic acid

[1] Thesis, Paris, 1899.
[2] J. Chem. Soc., 73, 796.

does not have the constitution assigned to it by Blanc. It should be represented by the formula (I) and camphoric acid by the formula (II):



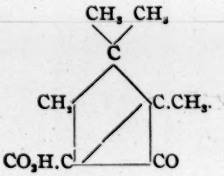
I.



II.

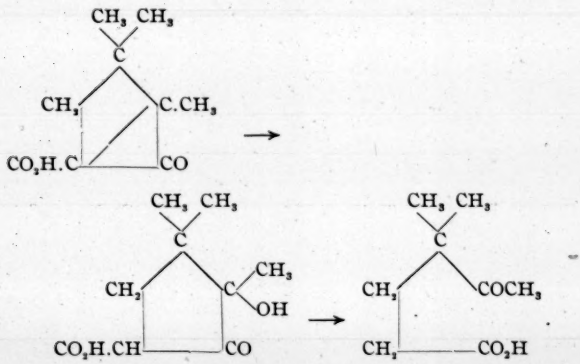
The reasoning adopted by the English chemist was as follows:

When isolauronolic (Noyes's campholytic) acid is oxidized with potassium permanganate, there is formed a keto acid, isolauronic acid, $C_9H_{12}O_3$, whose constitution must be represented by the formula

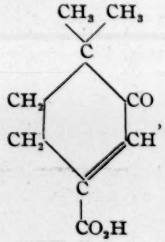


In fact, this acid, when reduced, gives an oxy acid, $C_9H_{14}O_3$ (dihydroisolauronic acid), which does not yield a lactone

and is therefore a β-ketone acid. Moreover, oxidation with chromic acid gives dimethylhexanonoic (dimethylacetylbutyric) acid, a reaction which Perkin explains as follows:

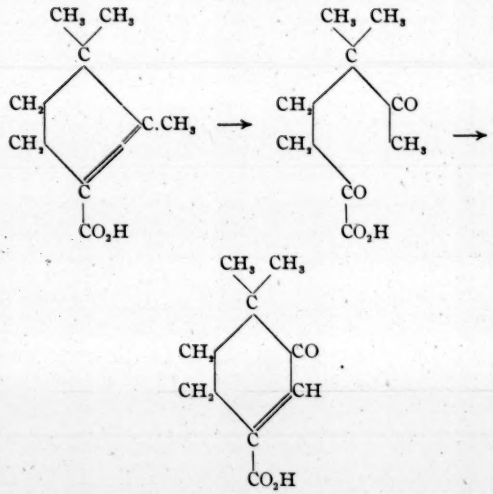


I had no difficulty in showing that this reasoning, as well as the experiments themselves, is vitiated by the gravest errors;[1] that isolauronic acid, far from having the formula assigned to it by Perkin, had, on the contrary, the structure represented by the formula

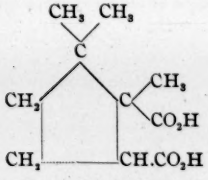


which was perfectly in accord with the formula for isolauronolic acid proposed and proved by me:

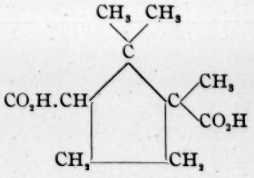
[1] Bull. Soc. Chim., [3] **21**, 830 (1899).



Consequently, Perkin's barely budded formula disappeared, and there remained but those of Bouveault and Bredt, with the greatest chances of probability in favor of the former:



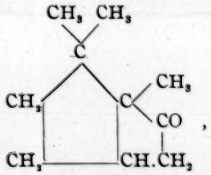
Bouveault's formula.



Bredt's formula.

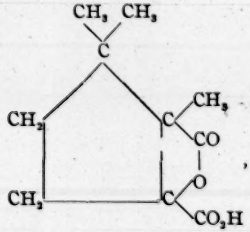
I say chances of probability and not of certainty, for although the most conclusive facts were in its favor (and I repeat that the constitution of isolauronolic acid was a perfectly definite argument), there remained a few points which

had not been cleared up with absolute satisfaction. In the first place it was difficult to see how camphor,



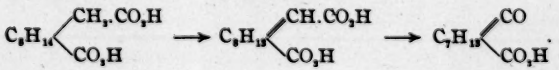
was converted into cymene and carvacrol; again, camphor itself, which must result from the closing of the chain in homocamphoric acid, would contain a tetramethylene chain, and no such example of ring formation was known.

On the other hand, the difficulty of explaining the lactone nature of camphanic acid,



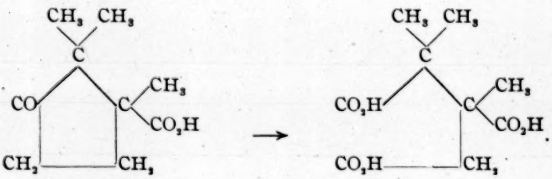
and the oxidation products of α-campholenic acid confirmed my belief as to the necessity of continuing these investigations.

Just at this stage of the problem, Lapworth[1] showed that homocamphoric acid can be brominated and that the bromo acid loses a molecule of hydrobromic acid to form an unsaturated acid which, on oxidation, is converted into oxalic acid and a keto acid, $C_9H_{14}O_3$, camphononic acid:



[1] J. Chem. Soc., 77, 1053.

This acid is stable and is not decomposed by distillation; it can therefore be only a γ-or δ-keto acid. Moreover, by oxidation it is converted into camphoronic acid, which proves its constitution:



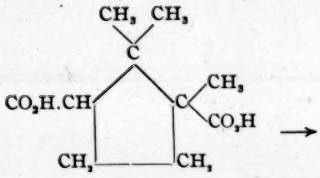
Camphononic acid. Camphoronic acid.

These observations, entirely in harmony with Bredt's formula and totally at variance with Bouveault's, led me to verify again the validity of the reasoning by which I had derived the formula for camphoric acid from the known constitution of isolauronolic acid. I was again unable to find any valid objection against it. If Bouveault's formula was incorrect, then some transformation must necessarily have taken place during the conversion of camphoric into isolauronolic (campholytic) acid.

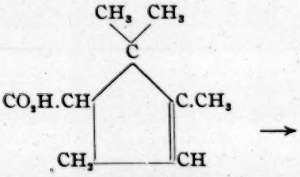
That this did take place I was, as a matter of fact, able to show. I pointed out,[1] simultaneously with Tiemann,[2] that isolauronolic acid is not the normal product of the decomposition of camphoric acid. The real normal product is a liquid acid (Noyes's *trans*campholytic acid) which is obtained by the action of nitrous acid on dihydroaminocampholytic acid. It is only when finally treated with dilute acids that this compound is transformed, quite easily, to be sure, into a solid crystalline acid (β-campholytic, *cis*campholytic, isolauronolic acid).

This α-campholytic (Noyes's *trans*campholytic) acid is oxidized by nitric acid to dimethyltricarballylic acid, which proves its constitution and, consequently, the correctness of Bredt's formula for camphoric acid:

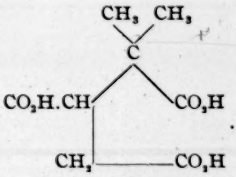
[1] Bull. Soc. Chim., [3] **25**, 68.
[2] Dict. Chim. Gén., **33**, 2935.



Camphoric acid.



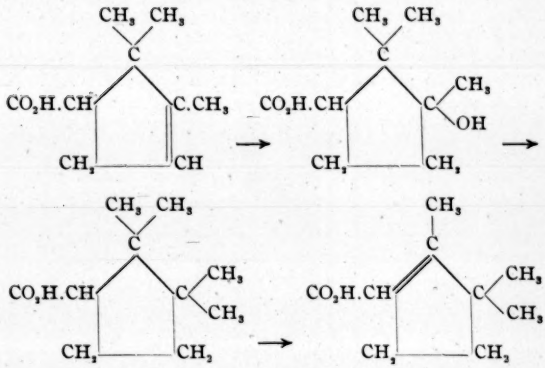
α-Campholytic acid.



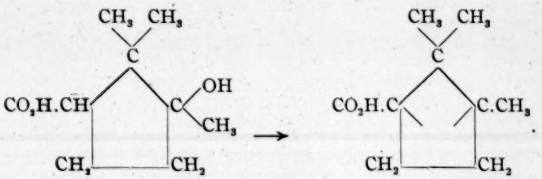
Dimethyltricarballylic acid.

The proof of Bredt's formula is thus due in part to those who had combated it. This is merely mentioned to show that the manifestation of the truth rises above all considerations.

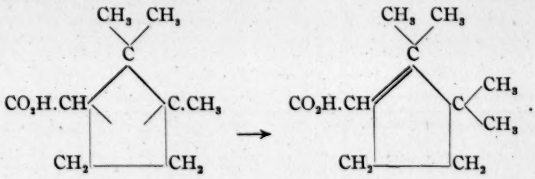
It remains to show how, starting from the constitutional formula for α-campholytic (*trans*campholytic) acid, that of isolauronolic (β-campholytic) acid can be explained. The mechanism of the pinacol reaction shows this very clearly.



The explanation proposed by Tiffeneau, although leading to the same result, is much simpler and more logical:



The molecule is thus thrown into a state of unstable equilibrium, and stable equilibrium is established in the simplest possible manner, *viz.*:



Such are the facts which marked the final adoption of Bredt's formula.

ATTEMPTS TO SYNTHESIZE, AND THE SYNTHESIS OF, CAMPHORIC ACID.

We have just seen the considerable difficulty which those chemists encountered who attacked the problem by analytical methods.

The solution which could not be obtained thus it was sought to obtain by the inverse method, the synthetical. This was a grave mistake, for synthetic investigations in this series are extremely difficult and require an immense amount of work, and it was not till the question had been completely cleared up by the analytical method that two syntheses of camphoric acid were worked out.

For these we are indebted to G. Komppa, on the one hand, and to W. H. Perkin, Jr., and J. F. Thorpe on the other. Of the second of these I shall say nothing except that it is extremely ingenious and that the chemists who effected it gave evidence of remarkable sagacity and patience. Having had occasion to repeat it, I convinced myself that it leads to the result claimed for it.

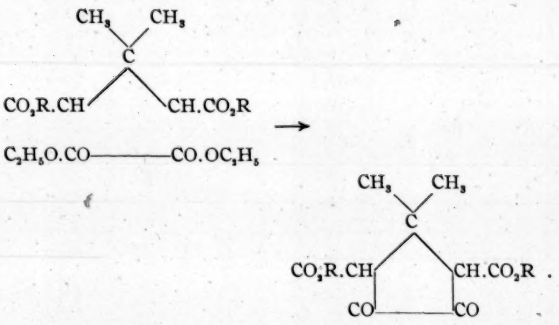
G. Komppa's Synthesis.[1]

Komppa's synthesis, the first in point of time, attracted considerable attention for, very unjustly, to be sure, the conclusive demonstration of the correctness of Bredt's formula was attributed to it.

Komppa's work, which was never published in detail and has not, in the last six years, passed beyond the stage of a preliminary communication (*vorläufige Mittheilung*), is based on the following facts:

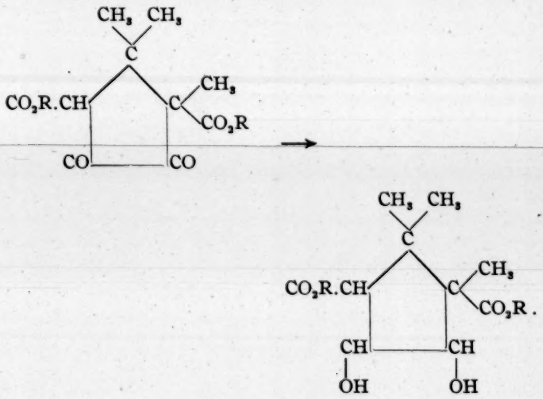
Condensation of oxalic ester with β,β-dimethylglutaric ester:

[1] Dict. Chim. Gén., **36**, 4332.

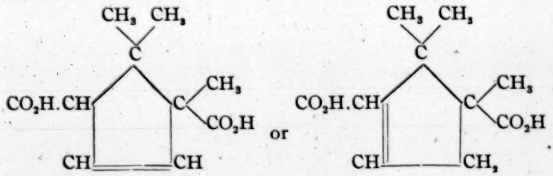


The diketoapocamphoric ester thus obtained is methylated by means of methyl iodide and sodium. The compound sought for is separated first as its sodium, then as its copper salt.

The methylated ester is then reduced with sodium amalgam in water solution in the presence of carbon dioxide:



The new product, dihydroxycamphoric ester, is saponified and heated with concentrated hydriodic acid, which gives an unsaturated acid,



The latter acid can add hydrobromic acid in acetic acid solution, giving a bromcamphoric acid which, by reduction with zinc dust and acetic acid, gives mesocamphoric acid and this, in turn, can be transformed into *cis-r*-camphoric acid.

Such a series of reactions supports with difficulty any serious scrutiny, and from the fact that Komppa has never given the details as to the procedures followed by him and since I have never been able to convert the first cyclic compounds into the diketoapocamphoric acid derivative, I shall consider Komppa's synthesis as nonexistant until the appearance of a detailed report will have enabled me to confirm the reality of a series of reactions which, on paper, offers no great chance of success. This is said merely with the intention of inviting Komppa to hasten the publication of his results.

I have finished this brief historical review of a problem which for several years deeply interested chemists. This question is now and has for some time been absolutely cleared up.

A single point remains in profound darkness; it is the mechanism of the reaction by which camphor passes into camphene, and *vice versa*. This subject therefore deserves the attention of those whom difficult investigations do not deter.

Perhaps I shall some day have the opportunity to take it up.

OBITUARIES.

CHARLES BENJAMIN DUDLEY.

Dr. Charles B. Dudley, Chief Chemist of the Pennsylvania Railroad, died of pneumonia after a very short illness on December 21st, 1909, at his home in Altoona, Pa. By his death chemistry loses one of its most enthusiastic supporters, science a devoted advocate, industry an important adviser, the country a patriotic citizen, and many in all professions a devoted and true friend.

Dr. Dudley was born at Oxford, Chenango Co., N. Y., July 14, 1842, of New England parentage. His early days were spent in attending the village school during the winter and in work upon the farm during the summer. In 1862 his patriotic spirit led him to enlist in the One Hundredth and Fourteenth Regiment of New York Volunteers, and he spent the greater part of the three succeeding years in the service of his country, taking part in seven battles and finally being wounded September 19, 1864, in the battle of Opequan Creek in the Shenandoah campaign. After his return from the war he continued his preparation for college at Oxford Academy. He entered Yale College and graduated with the class of 1871. The next year he spent in newspaper work in New Haven, and in this manner saved enough to enable him to pursue further studies in chemistry and physics in the Sheffield Scientific School, from which he received the degree of Ph.D. in 1874. The year following was spent as assistant in physics, under Prof. Barker, at the University of Pennsylvania. In the fall of 1875 he accepted the position of teacher of science in Riverview Military Academy, Poughkeepsie, N. Y., but remained only a month, leaving to accept the position of chemist with the Pennsylvania Railroad. From that time until his death he was continuously connected with this company. He was married April 17, 1906, to Mary V. Crawford, of Bryn Mawr, Pa.

Dr. Dudley was essentially a pioneer in the field of testing materials, and during his thirty-four years of service he accomplished an enormous amount of work, remarkable improvements were made for his company, and the world has adopted many of his recommendations as standards. A man of strong character, high ideals, clear, calm judgment, scholarly attainments, and a rare combination of qualities—charming personality, sympathetic, optimistic, he was unusually well

fitted for his task. After the organization of the laboratory, and establishing such routine testing as could be done at the time, he began a series of investigations upon the various materials used in railway practice. The investigations soon led to the introduction of specifications for the purchase of material, and these specifications, giving in some cases standard methods of analysis, have been widely copied, and have been very largely adopted as standards throughout the country. In this pioneer work, and always in all subsequent work, he was most zealous to protect the interests of his company, but at the same time he was always just to the manufacturer. He never expected the impossible of the manufacturers, but invariably led them persistently and tactfully toward his own high ideals. His views of the immediate needs of the Pennsylvania Railroad and the ultimate need of the world at large were so broad that he succeeded not only in safe-guarding the interests of his company and protecting the lives of its employees and passengers but in raising the standards of all the manufacturers having dealings with the company. The work of his laboratory on oils, paints and varnishes, bronzes and bearing metals, the various classes of steel used in locomotive and car construction, cast iron for car wheels, water examination, car ventilation and sanitation, the transportation of explosives, etc., marks an important epoch in the history of applied chemisty in America.

The first work which attracted attention to the Altoona laboratory was upon "The Wearing Capacity of Steel Rails in Relation to Their Chemical Composition and Physical Properties," which appeared in 1881. This paper not only had the effect of bringing to the attention of the world the need of a good quality of steel for rails, but what the author most desired, it focused the attention of metallurgists and engineers upon an important problem, and created discussion. Such discussion, whether favorable or otherwise, Dr. Dudley always thought of the greatest importance and he gladly welcomed it. Subsequent papers on the constitution of cast iron, and upon the qualities of bearing metals led to improvements in the manufacture of car wheels and to increased efficiency in bearings. Papers on oils, paints, and analytical methods all seemed to show the need for the improvement of these products or the means of testing them. Unfortunately, the publications from this laboratory were all too few because of the pressure of routine work in most varied fields, but part of his wonderful experience is related in his presidential addresses before the American Society for Testing Materials, and in discussions before this and other societies.

He was always an active worker in the interests of the American Chemical Society, for some time a councilor, and for two years president of the society. He was also a member of the English, French and German chemical societies.

Since 1902 he had been president of the American Society for Testing Materials, and last August, at the Stockholm meeting, was elected for a term of three years president of the International Society for Testing Materials. Of the former society he had been the heart and soul. His presidential addresses were models of their kind, and as presiding officer he brought out full discussion, and by his geniality and tact harmonized all interests.

Dr. Dudley was also president of the Bureau of Safe Transportation of Explosives and other Hazardous Materials of the American Railway Association, and gave much of his time during the past two years to the study of explosives and their safe handling in transportation. The catholicity of his tastes and his wide interests is shown in the large number of societies of which he was a member. He belonged to the American Societies of Civil, Mechanical, Mining, Sanitary and Electrical Engineering, the American Philosophical Society, American Historical Society, Society for the Promotion of Engineering Education, American Public Health Association, the Iron and Steel Institute of Great Britain, and others.

Dr. Dudley accomplished a great work. He was a broad-minded, widely educated man of simple and refined tastes, a true and faithful friend, and he was beloved by all who had the privilege of knowing him. HENRY FAY.

JAKOB VOLHARD.

Jakob Volhard, professor at the University of Halle, died on the 14th of January in his 76th year. He was a many-sided man; as investigator, as teacher, as editor and as biographer he showed great ability.

Volhard was born in Darmstadt, June 4th, 1834. His father was a lawyer and an intimate friend of Liebig, whose influence led young Volhard to the study of chemistry. Entering Liebig's laboratory in Giessen, in 1852, he studied under Liebig, Will and Kopp, receiving his doctorate in 1855. After working with Bunsen in Heidelberg for some time, he became Liebig's assistant in Munich, but in 1860 joined A. W. von Hofmann, in London. His studies of substituted ureas was made in Hofmann's laboratory. In 1862, while working in Kolbe's laboratory in Marburg, he published his

well-known synthesis of sarcosine. In 1863 he became privatdozent in Munich with Liebig, who assigned to him the lectures in organic chemistry. In 1868 he published the synthesis of creatine. He was made professor-extraordinarius in 1869.

After Liebig's death Adolf von Baeyer was called to Munich to reorganize the chemical department, and the new laboratory was built; it was the largest and best equipped at the time, and students poured in. The inorganic department was given to Volhard, and a new chapter of his life-work began. His studies with Bunsen bore fruit; turning his back upon organic chemistry, his lectures, his teaching and his private work were given to inorganic, and specially to analytical chemistry. His volumetric methods for the determination of silver, his introduction of ammonium sulphocyanide in volumetric work, his determination of manganese and his iodometric determination of sulphurous acid are now classic methods known in every laboratory.

It was, however, not as investigator, but as teacher, that Volhard showed his greatest power. Those who had the privilege of studying under his guidance during this period felt the constant inspiration of his teaching in the laboratory; his lectures on that usually dull subject, analytical chemistry, were masterly, and the students listened with breathless interest. His little book, "Introduction to Chemical Analysis," written at this time, is still in use in many German and some American laboratories.

It may be asked, if Volhard was so great a teacher of inorganic chemistry, where are his pupils? At this period nearly all young men of ability preferred organic chemistry as life-work, and their contact with Volhard was brief. Of the few who elected inorganic chemistry, the most promising perhaps were Clemens Zimmermann and Gerhard Krüss. Both died very young, each having done enough to earn a place in the annals of analytical chemistry and to show the result of Volhard's teaching.

In 1871 Volhard succeeded Liebig as editor of the "Annalen," and continued this work with energy and success for nearly forty years. In 1879 he accepted the chair of chemistry at Erlangen, and in 1882 went to Halle, where he conducted the chemical department till 1908, when he retired from active work.

Volhard's marked artistic and literary taste was of service in his biographical work. In 1870 he published "The Foundation of Chemistry by Lavoisier," and in this his anti-French

and strong German feeling is clearly shown. In 1902 he wrote his beautiful life of Hofmann and in 1909 he published his great biography of Liebig, a delightful book which has received the highest praise from all critics.

Volhard's personality was marked; his frame was almost gigantic; his noble leonine head towered above ordinary men. Students first approached him with a sensation of fear, which soon gave place to admiration. Those who knew him well delighted in his conversation replete with wit, humor and knowledge, no matter what subject was broached. He was the last of the distinguished pupils of Liebig and Liebig's contemporaries—the last of the old guard. E. RENOUF.

REVIEWS.

VERHALTEN DER WICHTIGSTEN SELTENEN ERDEN ZU REAGENTIEN. Zum Gebrauch im Laboratorium. VON DR. JOS. V. PANAYEFF, vorm. Dozent am Chemischen Laboratorium Fresenius zu Wiesbaden. Halle a. S. : Druck und Verlag von Wilhelm Knapp. 1909. pp. iv + 83. Price, M 3.60.

This little book is well characterized by its title, which in itself is a practical review of its contents. Dr. von Panayeff has gathered together and given with some detail the action that takes place when soluble zirconium, thorium, cerium, praseodymium, neodymium, lanthanum, yttrium and erbium salts are treated with reagents. The compilation appears to have been accurately done by one familiar with the work from close personal observation, and some reactions original with the author are added. Each metal considered is first carefully described in the elementary stage so far as it has been obtained pure, but no serious attempt is made to point out methods of separation. The book is just what it pretends to be. CHARLES L. PARSONS.

A SHORT HANDBOOK OF OIL ANALYSIS. BY AUGUSTUS H. GILL, S.B., Ph.D., Associate Professor of Technical Analysis at the Massachusetts Institute of Technology, Boston, Mass. Fifth edition, revised and enlarged. Philadelphia and London: J. B. Lippincott Company. 1909. pp. 179. Price, $2.

The fifth edition of Gill's "Handbook of Oil Analysis" with its revision to include present practice will be welcomed by all who are interested in the examination of oils, for the usefulness of the previous editions has been widely appreciated. It is a great convenience to have at hand, in a concise form, such a collection of well-tried methods of tests and examination, but sufficiently comprehensive in its scope for ordinary

practical use. Besides the methods of analysis, mineral, animal, and vegetable oils are described as to their source, properties and uses. The appendix includes well-selected tables, a useful description of reagents, and a statement of commercial specifications.

The author's opinion as to the doubtful value of frictional journal tests will doubtless not be shared by those who appreciate their practical advantages. CHARLES F. MABERY.

ELEMENTARY MODERN CHEMISTRY. By WILHELM OSTWALD, Emeritus Professor of Chemistry in the University of Leipzig and HARRY W. MORSE, Instructor in Physics in Harvard University. Boston, New York, Chicago, London: Linn & Co. pp. x + 290. Price, $1.

Every book by Ostwald has a touch of his genius and differs from the ordinary run of text-books. This little volume seems to be intended for schools; it would form an almost ideal preparation for college work. Following the ordinary sequence of elementary inorganic text-books, Ostwald explains combining weights, atoms, molecules, gram-molecular weights, electrolysis and electrolytic dissociation in such a lucid and simple way that any intelligent school boy would follow his reasoning. Indeed, the book would suffice admirably for a first year's college work in connection with lectures and some book for reference and study giving additional facts; this would be necessary, because—perhaps to gain space for theory—the amount of chemical fact in the book is reduced to a minimum: one example may suffice; steel is so defined as to lead to the belief that it is a substance differing from wrought iron or cast iron by its carbon percentage alone; nothing is said of it properties.

The book is illustrated with admirable diagrams and also contains portraits of Priestley, Ramsay, Dalton, Faraday, Berthelot, Bunsen, Willard Gibbs and Berzelius.

How much of the praise given Ostwald is due to Mr. Morse is doubtful, as the degree of Mr. Morse's collaboration is not stated; the qualities praised, however, are equally noticeable in Ostwald's former elementary book, "Conversations on Chemistry." E. R.

EIGHTH INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY.

On the evening of February 3, 1910, an informal gathering took place at which there were present, among others, most of those to whom had been delegated the task of providing for the creation of an organization for the Eighth

International Congress of Applied Chemistry, by the London Congress last June; a representative of the Association of Manufacturing Chemists, the American Chemical Society, the American Electrochemical Society, the Society of Chemical Industry were each also present at this informal meeting.

The concensus of opinion was that the greatest success could be expected only if the most effective system and mode of organization could be had, and if each and every chemist in the United States could be made to feel that he himself directly or indirectly, through his professional, business or educational affiliations, had a personal share of responsibility in the conduct and management of the Congress from its very start and to its very end. This was regarded as the proper and correct guide in proposing any plans or schemes of organization.

The Eighth Congress is to convene in 1912, with Professor Edward W. Morley as honorary president and Dr. W. H. Nichols as acting president, at a time and place to be determined by the Organization of this Congress. The most important part of the Congress, in fact that by which its value and real success will be measured, is the amount of original matter, both scientific and technical, which it will be able to present to its members. To this end, every chemist in America who has or may have any original matter to present to this Congress should begin without delay to prepare such matter, and have it in shape so that it may be presented to the Congress in ample time for proper printing, classification and distribution to members and the technical and scientific press.

The Congress, being held in the United States, will with a great deal of right and naturally look to a very good showing from the chemists of the United States, and every chemist in this country, which is to be host to our foreign colleagues, should constitute himself a committee of one to get from himself, or from his friends, as much scientifically or technically valuable material as possible, so that the proceedings and publications of the Eighth Congress may correctly reflect the true mental attitude of the chemists of the United States towards their profession, both as a pure science and as a part of the industrial activities of this country.

It is the hope that the Program Committee will be able to begin its activities effectively before the close of 1910, but in the meantime it behooves every chemist in the United States actively and energetically to consider how and in what way he can best contribute to the success of this Congress, and particularly in the direction of papers and communications

to the Congress embodying the advance in this field since June, 1909, the date of the last Congress.

At a meeting to be held in April or May, 1910, by those charged with the duty of providing suitable organization for the Eighth Congress, some definite action as to such organization may be looked for. Those who have that responsibility are making every effort to get as many suggestions as to divisions of organization, mode of organizing and membership of the organization as possible. Every one interested in having this organization on as broad foundations as possible is earnestly invited to present any suggestions that may be helpful in that direction, in writing, by the middle of April, 1910, so that all these suggestions may be properly classified and collated and put in condition for most thorough consideration before the meeting above referred to actually takes place. Such communications may be addressed to the Temporary Secretary, Gr. B. C. Hesse, 90 William Street, New York City.